Final Report

Characterization of Restoration Mortars For Fort Sumter National Monument and Degradation of Mortars by Sea Water And Frost Action

by

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Executive Summary

The focus of this research was determining the chemical solution or leaching by sea water from restoration mortars for use at Fort Sumter National Monument (FSNM) and for other masonry structures such as Third System fortifications and lighthouses built during the era of natural cement construction in the United States (roughly 1840-1900). The results are also germane to salt interaction in mortars resulting from masonry saturation by rising damp.

It was found that the mortars of this study containing Rosendale natural cement selectively absorb or "take up" ions of magnesium, chloride, and sulfate when immersed in sea water, but they also dissolve or leach species of calcium, potassium, and sodium. All of the mortars of this study exhibited weight loss indicative of corrosion loss in sea water, with mixes not containing lime exhibiting the highest corrosion weight loss. By contrast, the mixes only containing Rosendale cement and sand exhibited the lowest calcium solution on sea water immersion.

A central issue for restoration mortars used where salt intrusion is likely is calcium solution, as calcium solution has been shown to cause "brick scaling" or cryptoflorescence damage to bricks in the masonry walls. This was particularly noted at FSNM on faces of the structure pointed with Type O masonry mortar that are now exhibiting significant scaling damage. Since most restoration strategies include a mandate to "do no harm", the lowest calcium leaching or loss in the presence of sea water intrusion is a very significant criterion. Therefore, lime free or low lime content mortars with natural cement are preferred for restoration since they have the lowest potential to cause brick wear by scaling.

Restoration specialists have long recognized that it is a mistake to use "hard" portland cement containing mortars in pointing repair of "soft" historic bricks, as this practice results in facial disintegration of the old bricks. Now, this research has shown a chemical leaching criterion of importance for restoration to use in concert with decisions on Modulus of Elasticity for repair mortars.

The research strongly suggests that mortars with high contents of Rosendale cement and with minimal lime in their composition exhibit superior resistance to freezing and thawing as compared to mortars with lower cement content or those gauged with more than a *de minimis* content of lime (as considerably less than one quarter part of lime to one part of cement). Therefore, optimal mortar compositions with natural cement for sea or ground water contact are the same as those for frost prone geographic zones.

The results of this research are in agreement with knowledge gained through the ages in situations where masonry is usually immersed in sea water. For example, in Venice (Italy) pozzolanic (natural) cements have been used in restoration mortars in areas of sea water impingement and in areas of rising damp, with lime mortars used in higher building elevations for restoration. For Third System fortifications, lighthouses, and other structures where salt intrusion is likely and where Rosendale cement is preferred for restoration, the mortars should contain little or no lime to ensure no harm to the bricks in the masonry structure.

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Introduction

Rationale for this Research

Recent forensic analyses of masonry materials at Fort Sumter National Monument (FSNM) revealed chemical interactions between masonry materials and sea water that resulted in corrosion loss of mortar and scaling loss from brick faces, the latter induced by solution of mortar constituents with dissolved species damaging bricks through a process known as cryptoflorescence[1].The interaction between sea water and clay brick masonry has been described by Labelli and coworkers, who find that chloride ions in the water renders the carbonated lime in mortars as soluble[2]. This dissolution of mortar constituents leads to "corrosive loss" of mortar components and to movement of dissolved calcium from the mortar into the bricks.

Corrosion is a term usually not associated with salt action on brick masonry, but the effects of these chemical interactions are well known. A classical definition of corrosion is "the disintegration of an engineered material into its constituent atoms due to chemical reactions with its surroundings"[3]. The term corrosion is usually applied to metals, with one well-known example as rusting of iron or steel. However, corrosion is observed in polymers and ceramic materials, although the process is usually referred to as *degradation*. Degradation, however, can include mechanisms of destruction not necessarily involving chemical processes – for example erosion and frost damage. In the absence of mechanical processes leading to destruction of materials, the preservation and restoration community should apply the term *corrosion* to masonry in cases of salt related degradation.

Salt attack in brick masonry is well known in lower courses of brickwork on buildings well distant from the sea. Warren describes "chemical attack" related to moisture movement, where the moisture contains dissolved ground salts with movement from ground level upward by "rising damp"[4]. The degradation of the wall is seen as mortar loss and scaling loss from bricks due to rising damp, and this is essentially a corrosion process similar to the case of sea water corrosion of masonry.

Labelli describes how salts dissolved from mortar can lead to damage in bricks (reference 2). The intruding water solution from the masonry surface saturates the mortar leading to subsurface solution of calcium (and other atomic species). In drying periods, the salt-laden water moves both through the mortar and the bricks toward the masonry exterior, depositing the dissolved species (salts) as the water is evaporated. The crystallization of the salts is expansive in

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[1] Denis A. Brosnan, *Characterization and Forensic Studies of Construction Materials from Fort Sumter National Monument*, Report Prepared Under the Piedmont – South Atlantic Coast Cooperative Ecosystems Studies Unit Task Agreement For The National Park Service (2010).

[2] B. Lubelli, R. van Hees, and C. Groot, *The role of sea salts in the occurrence of different damage mechanisms and decay patterns in brick masonry*, Construction and Building Materials 18 (2004) 119-124.

[3] See http://en.wikipedia.org/wiki/Corrosion.

[4] John Warren, *Conservation of Brick*, ISBN 0 7506 3091 4, (1999), 151-163.

nature, and subsurface stresses cause thin layers of brick to be lost in the process known as "salt scaling"[5].

For restoration of masonry, there is a concern for use of *authentic materials* to match the *aesthetics* of the structure being repaired, but there is also a directive to "do no harm" to the historic fabric. For example, use of "hard" masonry mortars is avoided with soft historic bricks in masonry pointing, as it is well known that hard "inelastic" mortars cause decay of softer or more elastic bricks[6,7]. However, there is less recognition of chemical concerns for restoration with regard to mortars. Therefore, a major purpose of this research is to emphasize mortar solubility as an important consideration in restoration of historic structures.

Natural cements were used in masonry construction of most Third System Fortifications to include FSNM. The Chief Engineer of the U.S. Corps of Engineers, General J. G. Totten, experimented with "Roman cement" in Europe and later dictated use of a natural cement from Rosendale, N.Y., for use in the Fort constructions in the 1800's[8]. In some cases, the Rosendale cement was "gauged" with lime to reduce costs and facilitate construction using locally available materials[9]. It is a *key point* that the solubility of lime from mortar in sea water as a function of mortar mix composition is not reported previously in restoration literature. Therefore, a major purpose of this report is reporting solubility from candidate restoration mortars in situation of exposure to sea water.

The main soluble species of interest in masonry mortars is calcium (Ca). While calcium solubility is necessary, for example, in the setting process of contemporary portland cement mortar or masonry cement mortars, it is that the *quantity of soluble calcium* should be limited to the minimum necessary to meet strength related specifications, such as those in ASTM C270[10]. Calcium in excess of this minimum, especially in the presence of sea water, leads to efflorescence and cryptoflorescence, with potential to damage the historic fabric.

A further purpose of this research was providing engineering information to make this research generally valuable to the entire restoration community. The freezing and thawing durability of the restoration mortars was evaluated to provide information for restoration of masonry buildings and structures in frost prone localities not necessarily adjacent to the sea. Strength information was determined on masonry assemblies using the restoration mortars of this

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[5] If deposition of dissolved salts is limited to the immediate masonry surface causing discoloration, the process is known as *efflorescence*, ands scaling is usually not observed.

[6] *The Secretary of the Interior's Standards for Rehabilitation and Illustrated Guidelines for Rehabilitation of Historic Buildings* (U.S. Department of the Interior, The National Park Service (Reprinted 1997).

[7] R. Mack and J. Speweik,"Repointing Mortar Joints in Historic Masonry Buildings", *Preservation Brief 2, The National Park Service*.

[8] Michael P. Edison, Editor, *Natural Cements*, ASTM STP 1494 (2008).

[9] The term "gauged" means mixed with (lime) to reduce cost and possibly improve workability/consistency.

[10] ASTM C270, *Standard Specification for Mortar for Unit Masonry*, The American Society for Testing and Materials.

study so that persons interested in design/repair and modeling of historic buildings have information needed for their work. The approach of this study involves sophisticated analytical techniques that are well-described in the literature[11].

Goals of this Research

1. Establish the relationship between mortar composition and durability of bedding and pointing mortars for historic masonry restoration. Durability refers both to salt related corrosion/expansion and to freezing and thawing durability. The focus is on natural cement compositions.

2. Characterize the experimental mortars with respect to engineering properties that affect the overall performance of the masonry to include: compressive strength versus curing time, elastic modulus, tensile splitting (Brazilian test or diametral compression), vapor permeance, and analytical characterizations.

3. Provide fundamental data on masonry assemblies of interest to structural engineers to include pier compressive strength, and flexural bond strength (bond wrench). *(This goal provides information that is now generally unavailable for Rosendale cement.)*

are the goals discussed in the conclusions?

[11] Dennis Dinger, *Characterization Techniques for Ceramists* (Morris Publishing, 2005).

Experimental Procedure

Mix Development

Materials, mixtures (mixes) and methods for research are provided in ASTM C1713, "Mortars for Repair of Historic Masonry." This standard allows for use of a variety of binder materials in mixes to include cements, hydrated lime, and lime putty with each material described by a separate Standard[12].The only cementitious binders used in this study were Rosendale natural cement and lime.

The term binder includes cement and lime materials[13], as cements set or gain strength through chemical reactions involving hydration and carbonation, while non-hydraulic limes, aka "air lime" or "lime putty", attain a set through reaction with atmospheric carbon dioxide (carbonation). Lime putty, i.e. low magnesium content calcium hydroxide in slurry form, and dolomitic air lime (high magnesium content powdered form) were used in this study.

The binder to aggregate ratio is set by ASTM Standards as shown in Table 1. The ratios specified cover a number of cementitious materials to include natural cement, portland cement, masonry cement, and mortar cement.

Table 1: Mix Proportions in Specifications

Standard	Minimum Binder to Aggregate Ratio (Volume)	Maximum Binder to Aggregate Ratio (Volume)
ASTM C1713	1:2	1:3½
ASTM C270	1:2¼	1:3

Contemporary masonry uses various proportions of cement and lime along with sand in portland cement – lime mortars (Table 2). In general, the highest strength mortar is Type S with compressive strength declining in the sequence Types M, S, N, and O. This also means that Type O mortar is the most elastic mortar mix (lowest modulus of elasticity[14]).

[12] Natural cement (ASTM C10); hydrated lime (ASTM C207); lime putty (ASTM C1489); and sand (ASTM C144 and C778).

[13] Lime includes non-hydraulic lime that attains a set by carbonation and hydraulic lime that attains a set by a combination of chemical reactions and carbonation. Only non-hydraulic lime was used in this study.

[14] The Modulus of Elasticity (MOE) is the ratio of stress to strain when a material deforms at stress below which permanent deformation or fracture takes place. Materials with a low value of MOE are more elastic, i.e. they exhibit larger deformation at a specific stress, than materials with a high MOE, the latter of which are considered as more rigid.

Table 2: Contemporary Mortar Mix Proportions

Mortar Type	Proportion cement (volume)	Proportion lime (volume)	Proportion sand (volume)
Type M	1	¼	3
Type S	1	½	4½
Type N	1	1	6
Type O	1	2	9

Mortars with Rosendale cement used historically and in contemporary restorations have the batch proportions given in Table 3.The compositions with natural cement generally mimic the binder to cement ratios for contemporary mortars (Table 1); however, the lime content varies from zero up to quantities exceeding about one part of lime per part of natural cement. Lime was used to reduce the cost of mortars containing Rosendale cement, and it *functionally* adds workability to the mixes so as to make them easier to use in masonry construction.

Table 3: Mortar Mix Proportions by Volume with Natural Rosendale Cement

Mix Design	Proportions Cement	Proportions Lime	Proportions Sand
Totten (historic mix) without lime	1	0	2 – 2¼
Totten with lime (Ft. Warren Bedding Mortar)	1	½	2½
FSNM, Left Flank[15]	1	2	4
FSNM Right Flank	1	4	9
Edison[16], Ft. Warren Actual	1	½	3¼
Edison, Forts Richmond and Tomkins	1	0	2½
Edison, Museum of Natural History Restoration	1	0.3	2.5
Edison, Ft. Jefferson Restoration	1	0	1.0 – 1½
Edison, Poughkeepsie Amory Restoration	1	0.7	3.6

[15] Denis A. Brosnan, *Characterization and Forensic Studies of Construction Materials from Fort Sumter National Monument*, Report Prepared Under the Piedmont – South Atlantic Coast Cooperative Ecosystems Studies Unit Task Agreement For The National Park Service (2010).
[16] Michael P. Edison, *Proportioning Natural Cement Mortars*, Presented at The American Historic Cement Conference, New York (2011).

In order to establish mixes for use in this research, an experienced mason observed mixing of Rosendale cement, lime, and sand in various proportions to establish consistency goals for the wet mix and to obtain the mason's evaluation of the mortars[17]. The method of Weiss and Schork was used as an analytical measure of mortar consistency[18]. Of particular interest was the time for mortar to attain a set condition in curing that would allow for de-molding of the specimen to be followed by further curing. A residence time for specimens to be cured in molds of two to five days "as needed" is provided in ASTM C1713.

In preliminary experiments, mixes containing a ratio of lime to cement greater than 1:1 did not exhibit sufficient strength in 5-14 days to allow for de-molding. Insufficient strength development in five days of curing (for de-molding) suggests that mixes with lime to cement exceeding 1:1 are practically not useful in repair; therefore, 1:1 was set as a maximum lime to cement ratio. This essentially means *useful* or *practical* Type O mortar batch proportions cannot be made using the Rosendale cement employed in this research.

The mason observed that mixes made with lime to Rosendale cement ratios of ½:1 to 1:1, within the constraint of binder to sand of 1:2¼, were of sufficient workability to be used in large construction jobs[19]. *It was obvious to the mason that adding a small amount of lime to the mixes of Rosendale cement and sand had a profoundly beneficial effect of improving the workability of the mortar for construction.* These observations seem to be reflected in contemporary practice (Table 3). The actual mortars at FSNM do not fit within these constraint proportions suggesting that the mixes actually used in the field varied from the directives of the Corps of Engineers. The result of the mix development phase of this research provided the mortar compositions in Table 4.

Table 4: Mix Proportions by Volume for this Research

Mix	Proportions Cement	Proportions Lime	Proportions Sand
No Lime A (Proportions in C10)	1	0	0.6
No lime B (Totten Proportions)	1	0	2¼
Low Lime	1	½	1½
Higher Lime	1	1	2

[17] Mr. Bryan Light of the Brick Industry Association provided assistance on mix evaluations.

[18] Norman Weiss and Jennifer Schork, *Rosendale and French Lime Mortars*, Presented at The American Historic Cement Conference, New York (2011).

[19] Masons require both good workability and acceptable mortar board life, as quick or flash setting renders a mortar as unusable. By contrast, excessively slow setting hinders masonry construction as mortars must be able to bear the weight of successive layers in brickwork.

Experimental Approach

The materials chosen for this study included Rosendale cement, lime as lime putty[20] or hydrated dolomitic lime[21], and sand[22]. Lime putty was used as it was commonly used in construction in the 1800's. Mixes with dolomitic lime were used to determine if the magnesium content of the lime in those mixes affected the interaction of the mortar with sea water.

Because pointing of mortar in historic masonry structures is required for restoration, mixes for manual and grout bag pointing were included in the experimental design. These mixes were made at a lime to cement ratio of ½ to 1.0 - to allow for a comparison of mortars with varying porosities in the series manual pointing (least water content), bedding mortar, and grout bag mortar (highest water content). The final mixes are provided in Table 5.

For the mixes containing lime putty, the batch proportions were adjusted for the moisture content of the lime. For example, for Mix 1 the *wet batch proportions* were adjusted by using an appropriate amount of lime putty to achieve the desired proportions on *a dry batch volumetric basis*. The pointing mortar mixes (Mixes 6 and 7) were only made using lime putty as a source of lime.

[20] Virginia Lime Works lime putty derived from calcination of limestone. Lime putty is a wet material essentially submerged under water as a cake to minimize carbonation prior to use. Preparing lime putty for masonry construction dates back to the Roman Empire.
[21] Graymont Type S dolomitic lime.
[22] Quartz sand meeting ASTM C778 as "Graded Sand" to mimic mortars used at FSNM.

Table 5: Mortar Mixes Used in this Study by Volumetric Propor

Mix No.	Comment	Relative Volume Rosendale Cement	Relative Volume Lime (Dry Basis)	R
C	ASTM C-10 Mix	1	0	0.65
1	Totten Type Mix	1	0	2¼
2	Low Lime (LP lime)	1	½	1½
3	Higher Lime (LP lime)	1	1	2
4	Low Lime (DL lime)	1	½	1½
5	Higher Lime (DL lime)	1	1	2
6	Manual Pointing (Like Mix 2)	1	½	1½
7	Grout Bag Pointing (Like Mix 2)	1	½	1½

(LP = lime putty and DL = dolomitic lime)

Production of Test Specimens

Cement and lime used in this study were characterized as to chemical analysis, mineralogical analysis by X-ray diffraction, and thermal analysis (to determine extent of hydration and/or carbonation). Then batches were converted from volumetric proportions to weight proportions to assure accurate laboratory batching.

Mixing was in a 4.5 quart capacity Hobart mixer *generally* following C305 with the procedure modified as below, as shown in Figure 1 (800 gram batches were used and the water content on each first batch of a particular mix was adjusted to meet the penetrometer specification). The penetrometer method was adopted from the work of Weiss and Schork (Reference 6) as a method to repeatedly meet the consistency goals established by the mason. In this work, a penetrometer goal of 2-4 mm penetration was established as the desired range in mortar consistency[23] (See Figure 2).

The mixing procedure was:

1. Place the dry batch in mixer and mix 1-minute prior to water addition.

[23] Penetration of the wet mix was measured in mm using a 12.44 mm diameter blunt penetrometer head of height 44.44 mm and weight 9.1 g.

2. Add 1/3 of anticipated water slowly. Mix two additional minutes. Scrape down the bowl.
3. Add the second third of the anticipated water. Mix 2 minutes.
4. Let the mix rest for 1-minute (Mixer OFF).
5. Add the balance of the water slowly. Observe the mix begin to "crawl" up the bowl. The mix will suddenly become paste-like. Add water cautiously and slowly. This should be accomplished in 2-minutes.
6. Measure the consistency using Vicat penetration. If it is too low, return the mix to the bowl and add a slight amount of water. Test for Vicat consistency again and continue to adjust until you meet the target penetration range.
7. Use all mixed material to fabricate test specimens (cubes or cylinders) immediately.
8. Label disposable cube molds with the mix number and a sequential cube number. Use a laundry marker (insoluble ink).
9. All molded cubes are immediately placed in the 100% relative humidity container (called the "curing room). The room should be 70°C ± 5°C. (Note that ASTM C305 allows a range of 68-81.5°F but requires relative humidity ≥50%).

Figure 1: Mixing of Test Mortars (Photograph No. 1861)

Figure 2: Mix Consistency Measurement Using the Penetrometer (Photograph No. 1873)

Mortar test specimens were produced as either 2" (0.78 cm) cubes or cylinders 4" (1.57 cm) diameter by 2" (0.78 cm) length. These were produced by slight tamping of mortar into molds using a small square Plexiglas ram to ensure good fill of the molds. Disposable polymer molds were lubricated using cooking spray prior to insertion of the mortar mix.

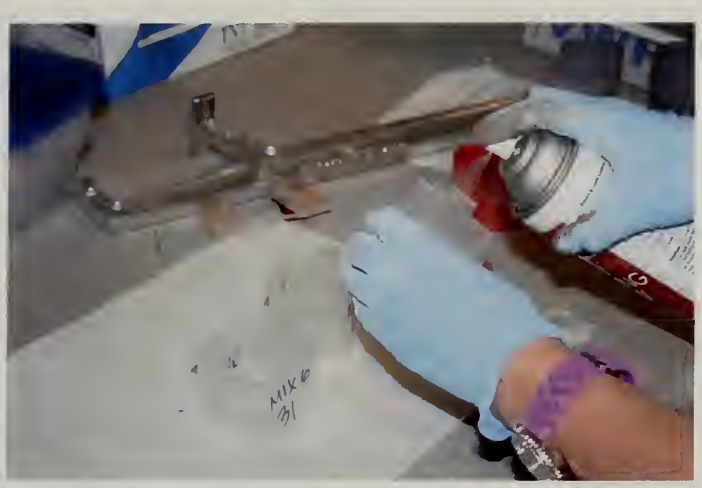

Figure 3: Applying Release Agent Prior to Mortar Insertion in Molds (Photograph No. 1868)

The mortars were initially cured at room temperature (70°F or 21°C) for a minimum of seven days at 100% relative humidity in polymer containers containing a large open pan of water (Figure 4). Mortars were then exposed to 100% relative humidity conditions at 120°F (49°C) with air recirculation and inspiration of ambient air to accelerate curing. The degree of curing was evaluated using a pH indicator solution on fracture faces according to the procedure of Weiss and Schork (Reference 6).

Figure 4: Curing Chamber for Initial Curing (Photograph No. 1882)

Characterization and Testing

Chemical and Mineralogical Characterization

Raw materials and experimental mortar specimens were characterized as to their chemical and mineralogical constitution using techniques provided in Table 6. These techniques are explained in literature[24].

Table 6: Chemical and Mineralogical Composition Tests

Test/Analytical Method	Abbreviation	Brief Description
X-ray fluorescence spectroscopy	XRF	X-rays generated by the specimen are analyzed to provide a chemical analysis of the specimen typically expressed as either chemical elements of as oxide species. In cement technology, the constituents are expressed in terms of content of metal oxides.
X-ray diffraction	XRD	X-rays are reflected or "diffracted" at characteristic angles allowing for an analysis of the mineral components of a material.
Thermal analysis	STA or DTA as "simultaneous thermal analysis" or differential thermal analysis"	Shows the existence of heat absorbing (endothermic) or heat releasing (exothermic) reactions on heating of a specimen so as to indicate the presence of certain minerals or species in a specimen. The decomposition of minerals is usually endothermic, while melting is always endothermic. The presence of calcium carbonate or "carbonated lime" in a mortar is revealed by the endothermic decomposition of $CaCO_3$ in the realm 700-800°C.
	TG or thermogravimetric analysis	Shows weight changes on heating. The decomposition of minerals usually results in a weight change.
	EGA or evolved gas analysis	Using infrared spectroscopy (in this study), gas releases, such as water vapor, sulfur dioxide, or carbon dioxide, are monitored during heating.
Specific surface area	SSA	Using gas adsorption techniques (BET Method), the surface area per gram of specimen weight is determined. The value reflects the particle size of the specimen, i.e. finer materials have a greater SSA than coarser materials.

The composition of mortar specimens was verified using the methods in ASTM C1324, *Standard Test Method for Examination and Analysis of Hardened Masonry Mortars*. In performing the analysis of mortar specimens, other techniques were used including XRF, XRD, and STA/TG/EGA.

[24] See, for example, Dennis Dinger, *Characterization Techniques for Ceramists* (Morris Publishing, 2005).

Physical Characterization

Physical characterization tests for mortar specimens and masonry assemblies are provided in Table 7.

Table 7: Physical Characterization of Mortar Specimens

Property	ASTM Standard	Specimen Size	Reason
Compressive strength	C109/C109M	2" cube	The compressive strength is a specified property in ASTM C10 and ASTM C270. It is the most important physical characterization method for a mortar specimen.
Linear expansion	NA	2" cube	The expansion of a cube side expressed as a percentage may indicate reactions with its environment.
Mercury intrusion porosimetry (MIP)	D4404	Small pieces.	Mercury is forced into the pores of a specimen under pressure, and the quantity of pores (the "porosity") and the sizes of pores (average diameter) are provided. The porosity is expressed as the percentage of the volume of the specimen that is accessible void space – such as accessible for water intrusion.
Tensile splitting	D3967	Cylinder L/D in range 0.2 to 0.75; In this research: 2" length X 3" diameter for L/D = 0.67	The tensile splitting (tensile strength) is a property useful in structural modeling.
Elastic Modulus (MOE)	C469	Mortar cube in compression.	An important characterization of mortar for repair of masonry by pointing.
Water Vapor Transmission (WVT)	E96	Not given	Measures the rate of permeation of water vapor by the mortar. WVT is an important property for restoration mortars, as mortar is expected to "breathe" to prevent water accumulation within masonry walls.
Pier compressive strength	C1314	5 unit pier, 4 joints; Mix 2 only.	The compressive strength of mortared assemblies or "prisms" is a useful property in engineering design and modeling of historic structures.
Flexural Bond Strength (Bond Wrench)	C1072	15 2-brick joints; Mixes C and 2 only.	The tensile strength of mortared assemblies is a useful property in engineering design and modeling of historic structures.

Sea Water Immersion Studies

Mortar cubes as-cured were immersed in simulated sea water[25] in individual polymer containers for scheduled immersion periods of 7, 28, 30, and 60 days (Table 8). During immersion, the mortar cubes either released species into the immersion fluid ("leachate") or absorbed species from that fluid.

The quantity of species either added (dissolved) or captured (uptake) from the immersion fluid was determined by chemical analysis of the immersion fluid. The chemical analysis techniques were ion chromatography (IC) and inductively coupled plasma/atomic absorption (ICP). In this sense, the method for chemical interaction between the mortar specimen and the leachate mimics the US EPA method for determining leaching behavior of solid waste materials, with the modification of using synthetic sea water as the "extraction fluid" (and in a static test environment)[26]. In these tests, the mortar cubes were rotated each day of immersion Monday through Friday, but the cubes were not rotated on Saturday and Sunday of each immersion week.

The results were expressed as quantity of species either released or absorbed per gram of the mortar cube weight – as the difference between the analysis of the impression fluid at a given immersion (soak) time and the initial composition of the immersion fluid. This method of differences clearly shows the solution of species as a positive number (contribution to the leachate) or absorption as a negative number (removal from the leachate).

Table 8: Immersion Fluid Composition

Constituent	Species	Concentration (g/l)
Sodium Chloride	NaCl	30
Magnesium Chloride	$MgCl_2$	6
Magnesium Sulfate	$MgSO_4$	5
Calcium Sulfate	$CaSO_4$	1.5
Potassium Hydrogen Carbonate	$KHCO_3$	0.2

Freezing and Thawing

The freezing and thawing durability of the mortars of this research was assessed using the testing method provided in ASTM C666, *Standard Test Method for Resistance of Concrete to Rapid Freezing and Thawing, Procedure A*, with the modification of visual observation of the disintegration of specimens as a function of freezing and thawing cycles rather than use of resonant frequency techniques (ASTM C215). In this research, three specimens of each Mix were tested. The test method is summarized as follows:

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[25] O 'Farrell, S. Wild, and B. Sabir, "Resistance to Chemical Attack of Ground Brick – PC Mortar Part II, Synthetic Seawater", Cement and Concrete Research 30 (2000) 757-765.

[26] See, for example, US EPA Method 1312.

- Specimens after curing are placed in a water bath such that the specimen is partially submerged to a depth not less than 1/32 inches or more than 1/8 inches. The specimens are protected from moisture loss after curing and prior to freezing them by covering them with impermeable materials.

- The specimen assembly is lowered in temperature from 40°F to 0°F and raising it from 0°F to 40°F in not less than two or more than five hours.

- At intervals, not to exceed 36 cycles of freezing and thawing, the specimen condition is assessed. In Procedure A, this is usually accomplished by resonant frequency techniques and additionally with length change measurements, the latter at the option of the investigator.

One pan of specimens prior to cycling is shown in Figure 5. Pans were placed in the commercial freezer cabinet (Figure 6) and the testing procedure began. After freezing, typically three cycles per day were achieved. The tests were interrupted periodically for inspection of the specimens allowing them to equilibrate with room temperature.

Figure 5: Specimens Immersed in Water prior to the C666 Test

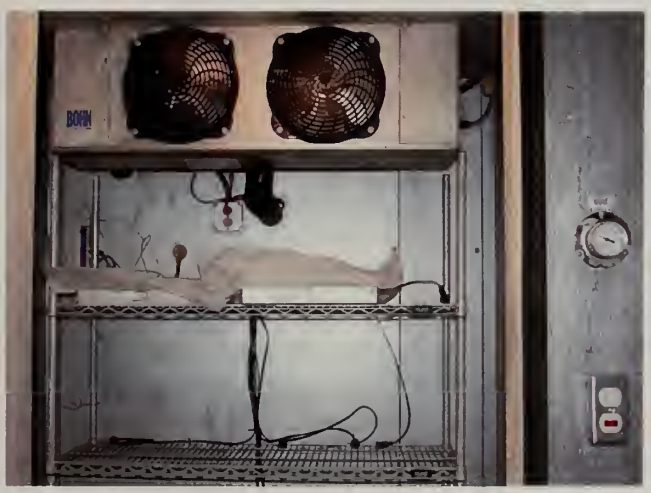

Figure 6: Covered Specimens in Pans in the C666 Test

Characterization of Materials and Mortar Mixes

Raw Materials

Natural Cement

The Loss on Ignition and chemical analysis of three sequential Rosendale cement shipments used in this research are given in Tables 9 and 10. Exploratory research was performed on the shipment labeled "A". All research including characterizations, sea water immersion/leaching, and freezing/thawing was performed using the shipment labeled "B". The shipment labeled "C" exhibited flash or quick setting and was not used in this research.

Table 9: Natural Cement LOI Data

Specimen/Lot	A	B	C
LOI (%)	10.56	9.60	11.87

Table 10: Chemical Analysis of Rosendale Cement by XRF

Major Constituents		Rosendale A	Rosendale B	Rosendale C
Al_2O_3	%	4.65	5.10	5.51
SiO_2	%	20.35	20.65	21.03
Na_2O	%	<0.5	<0.5	<0.5
K_2O	%	1.04	0.97	0.96
MgO	%	11.33	10.88	12.82
CaO	%	56.57	56.53	53.94
TiO_2	%	0.27	0.23	0.27
MnO	%	0.30	0.28	0.33
Fe_2O_3	%	1.89	1.80	1.87
P_2O_5	%	<0.05	<0.05	<0.05
S	%	3.02	3.04	2.78
Sum of Major Constituents	%	99.41	99.46	99.50

The XRD data for Rosendale specimens is given in Figures 7-9. A semi-quantitative analysis was performed for Specimens B and C. The major differences between Specimens B and C was that B contained higher contents of periclase (MgO), portlandite [$Ca(OH)_2$], and larnite (aka "belite" or $2CaO{\cdot}SiO_2$) while Specimen C contained a significantly higher content of lime and calcite. Free or uncombined lime can cause flash sets in calcium aluminate cements, and this may contribute to the faster setting characteristic of Specimen C as compared to Specimen B. The shape of the XRD curves at low angles indicates the presence of a glass component in the cements, but the glass content was not quantified.

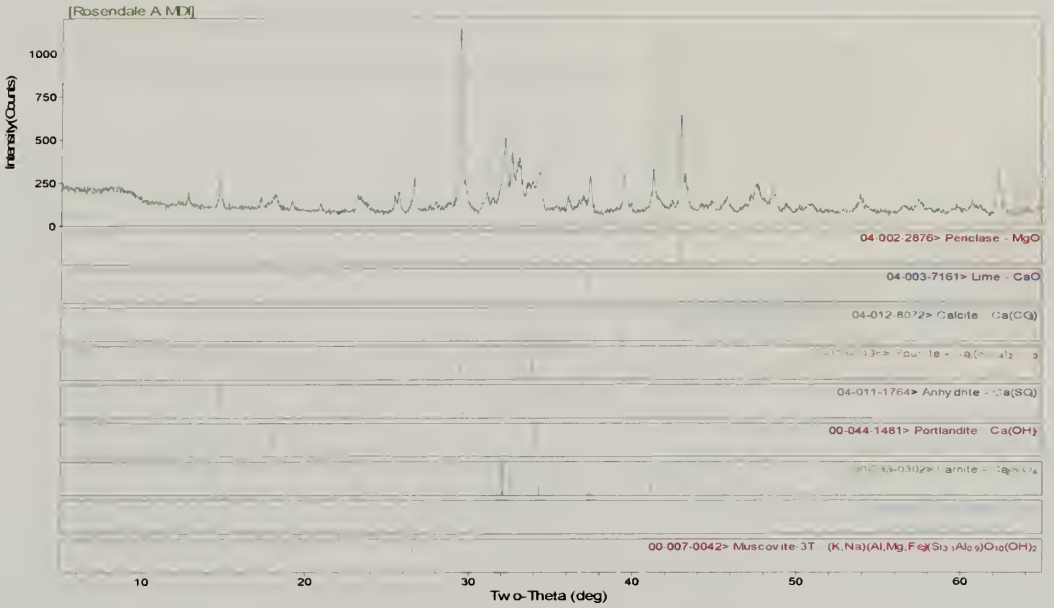

Figure 7: XRD Results for Rosendale Specimen A

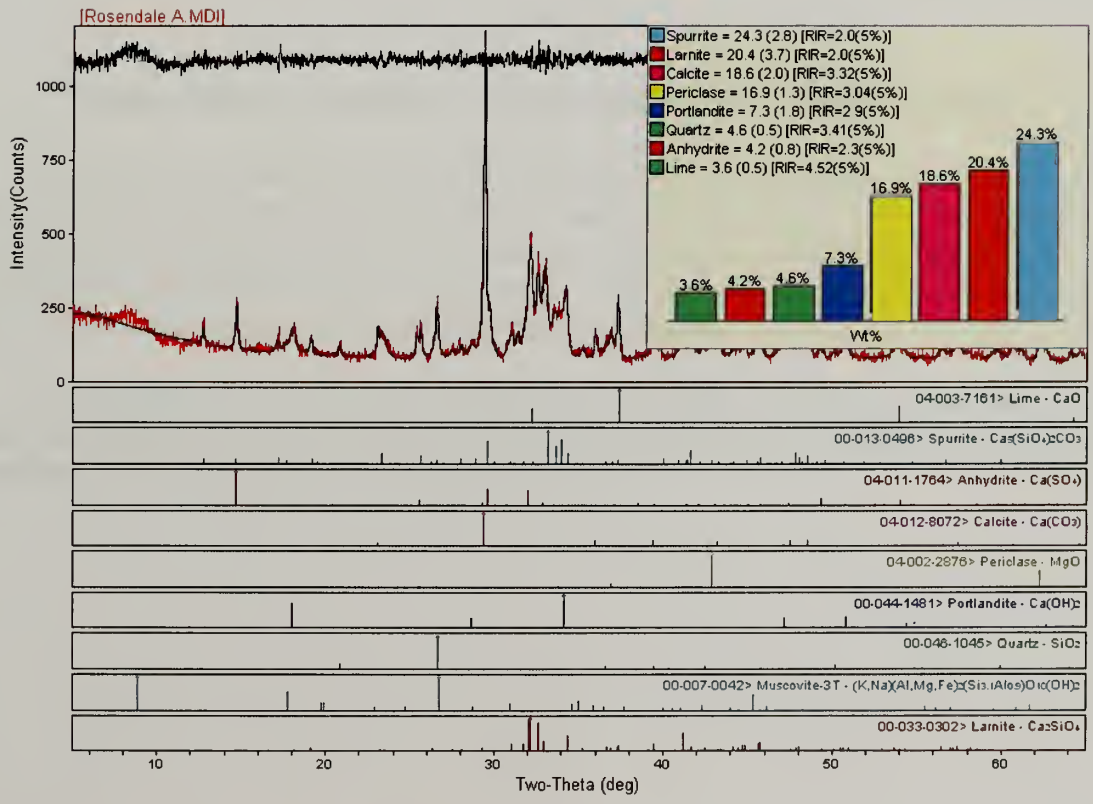

Figure 8: Semi-quantitative XRD Results for Rosendale Specimen B

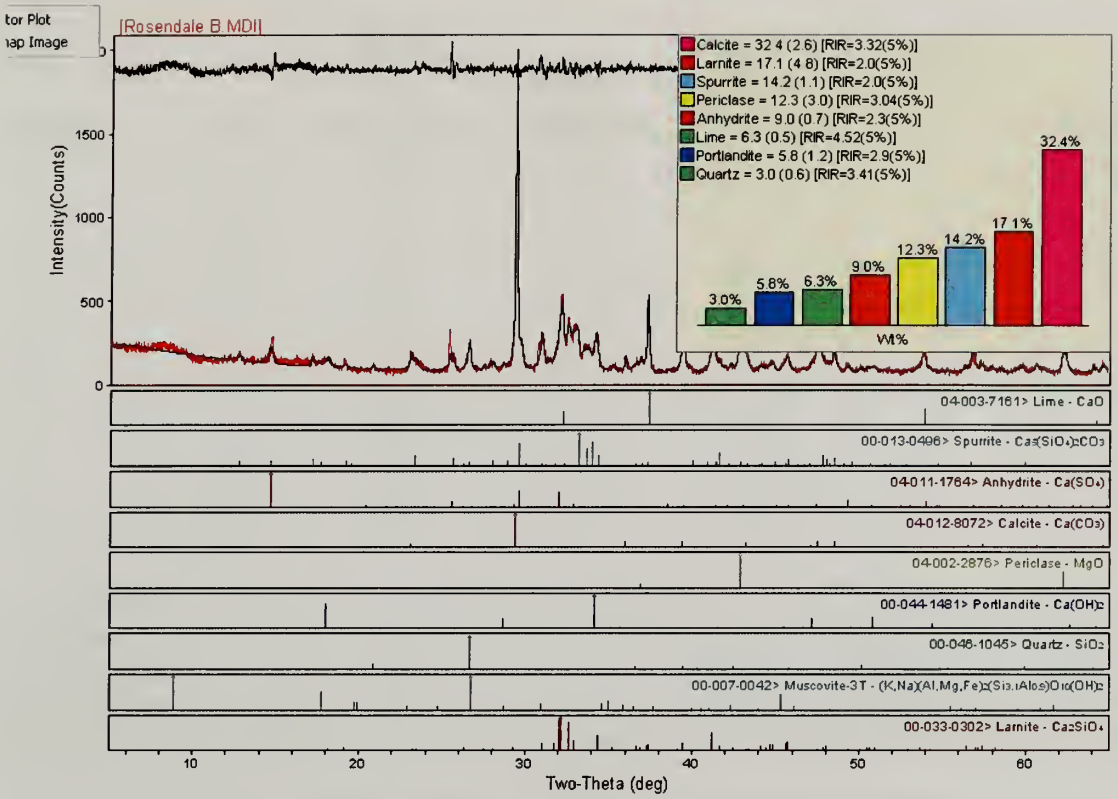

Figure 9: Semi-quantitative XRD Results for Rosendale Specimen C

The particle size analysis of the Rosendale specimens is provided in Table 11. The data suggests that the percentage of materials finer than 200 Mesh (75μ) could be different in the series of A (65.2%<44μ), B (77.4%<44μ), and C(54.6%<44μ). In obtaining this data, the cement specimens were removed from their 5-gallon pail, mixed in a low intensity lab mixer, and the sample was obtained by standard sample reduction techniques.

It is impossible to say that the difference in quantity of fine particles was the largest influence on setting rate. It can be said that this variation could be normal since the cement is not ground during manufacturing (as is portland cement).

Table 11: Sieve Analysis of Rosendale Cement Specimens

Sample	Sieve	Empty Sieve Weight [g]	Sample Weight [g]	Dry Sieve + Residue Weight [g]	Amount Retained [g]	% Retained
A	50	375.7	50.0	376.0	0.3	0.6
	100	371.2	25.0	374.0	2.8	11.2
	200	345.6	10.0	347.9	2.3	23.0
B	50	383.5	50.0	384.0	0.5	1.0
	100	371.4	25.0	374.3	2.9	11.6
	200	344.3	10.0	345.3	1.0	10.0
C	50	383.5	50.0	385.3	1.8	3.6
	100	371.5	25.0	375.7	4.2	16.8
	200	343.5	10.0	346.0	2.5	25.0

Densities of the cements are provided in Table 12, where the loose density value is the density obtained by filling a standard container without added vibration, and the tapped density is a similar procedure with compaction provided by striking or "tapping" the container. The average bulk density (tapped) of about 64 lb./ft^3 agrees well with a value provided by Edison[27] of 67.5 lb./ft^3. The tapped density of 64 lb./ft^3 was used in mortar batch calculations in this report.

Table 12: Bulk Densities of Rosendale Cement Specimens

Material	Sample	Loose Density	Tapped Density	Loose Density	Tapped Density
		g/cm^3	g/cm^3	lb./ft^3	lb./ft^3
Rosendale A	1	0.78	1.04	48.71	65.17
	2	0.78	1.00	48.73	62.69
	3	0.78	1.01	48.57	63.18
	Avg.	**0.78**	**1.02**	**48.67**	**63.68**
Rosendale B	1	0.76	1.02	47.16	63.52
	2	0.79	1.04	49.29	65.22
	3	0.79	1.01	49.02	62.79
	Avg.	**0.78**	**1.02**	**48.49**	**63.84**

[27] Michael P. Edison, *Proportioning Natural Cement Mortars*, Presented at the American Historic Cement Conference, New York (2011).

The specific surface areas of the cement specimens in Table 13 may provide more information on differences in setting rate, as Specimen C with the highest setting rate exhibited a greater surface area indicating there was more very fine material in this specimen.

Table 13: Surface Area of Cement Specimens

Material	Sample	BET Multipoint Surface Area
Rosendale Cement A	1	2.549
	2	2.610
	Average	2.579
Rosendale Cement B	1	2.4382
	2	2.4127
	Average	2.425
Rosendale Cement C	1	3.095
	2	3.4695
	Average	3.282

Neat cement pastes (cement and water mixtures after setting) were produced from specimens B and C, allowed to harden, and thermogravimetric analysis (TGA) was obtained (Figure 10). Differences in the weight loss are likely attributable to the differences in calcite content, with Specimen C exhibiting the highest amount of calcite (Figures 8 and 9).

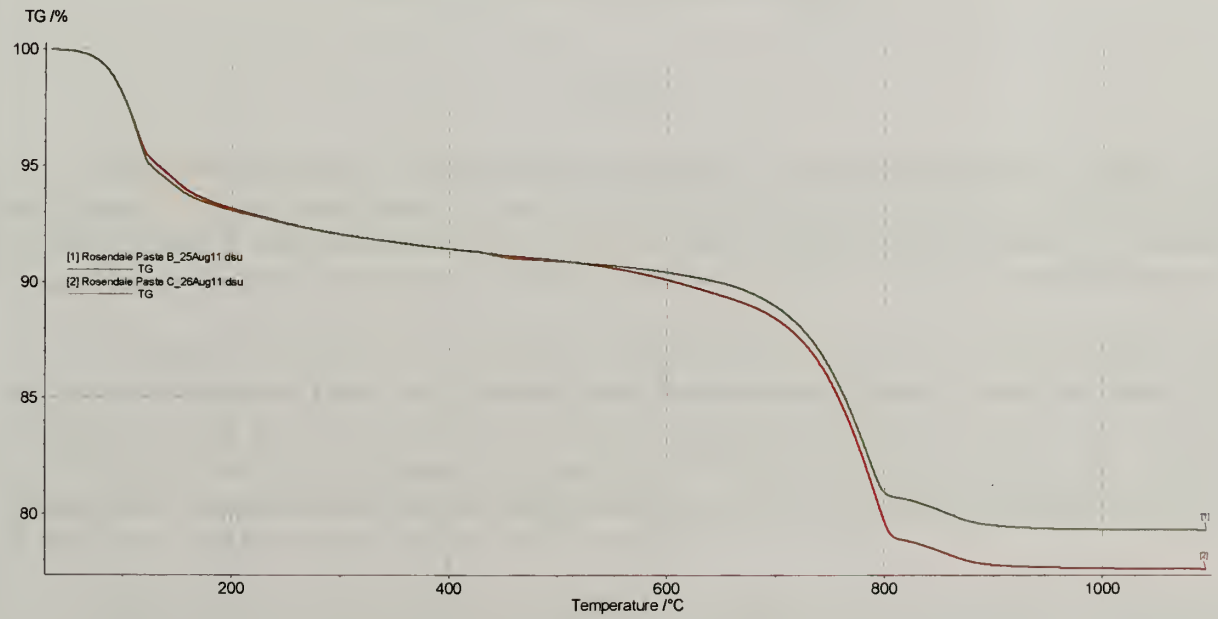

Figure 10: TGA of Cements B and C on Heating

The differential thermal analysis (DTA) analysis for Specimens B and C in Figure 11 shows a notable difference in an endothermic reaction at about 440°C (arrow). This endotherm is associated with the thermal decomposition of portlandite or $Ca(OH)_2$. The DTA quantification is not in agreement with the semi-quantitative XRD analysis that showed Specimen B to contain more portlandite than Specimen C, suggesting a possible error in the XRD estimation.

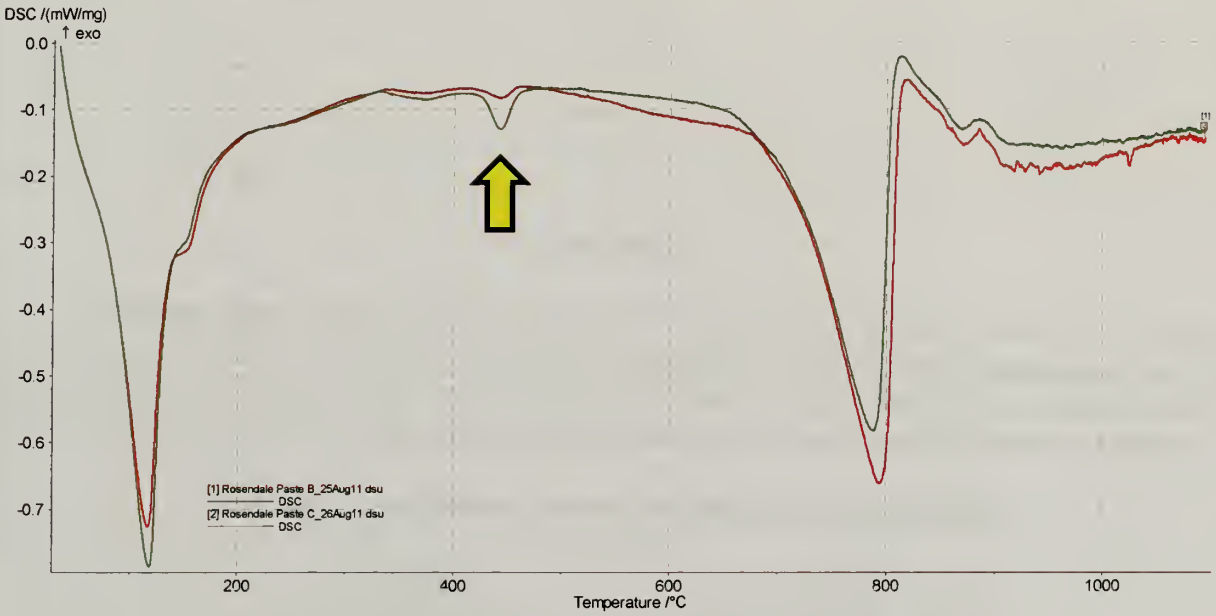

Figure 11: DTA of Specimens B and C

Sand

ASTM Specification C778-06 provides information in the section entitled "Scope", "This specification covers standard sand for use in the testing of hydraulic cements". Further in section 3.1.3 the Standard adds that the material is "silica sand, composed almost entirely of naturally rounded grains of nearly pure quartz, used for preparing mortars in testing of hydraulic cement".

To remove sand source as a variable in experiments, graded sand qualified under C778 was used in this study (Table 14). The sand color was white suggesting a purity of greater than 98% SiO_2 (quartz). The loose packed bulk density of the graded sand was measured as 95 lb./ft^3, a value higher than that expressed for "sand" of 80 lb./ft^3 in ASTM C1324. The vibration compacted or "tapped density" of the graded sand was 106 lb./ft^3, and an intermediate value of 98 lb./ft^3 was used in mix calculations in this research.

Graded sand was used in this study because the mason used in preliminary experiments expressed a preference of the consistency of mortars using this sand, and the particle size distribution best matched the natural sands used in Fort Sumter National Monument. This means that mortar specimens produced in this study cannot be compared in terms of physical properties

to the specifications in ASTM C10, since C10 requires use of "20-30 sand" in the standard compositions[28].

Table 14: Specifications for C778 Sand

Gradation, % passing sieve	20-30 Sand	Graded Sand
16	100	100
20	85-100	
30	0-5	96-100
40		65-75
50		20-30
100		0-4

Lime Putty

The lime putty used in this research was Virginia Lime Works Traditional Limestone Lime Putty, i.e. lime derived from burning of limestone[29]. The physical properties of the lime putty are given in Table 15. The wet bulk density of the putty falls below the minimum value of 80 lb./ft^3 given in ASTM C1489, *Standard Specification for Lime Putty for Structural Purposes.*

Table 15: Lime Putty Density, Moisture Content, and LOI

Property	Value
Bulk density (wet)	0.84 g/cm^3 (52.4 lb./ft^3)
Bulk density (dry)	0.46 (28.7 lb./ft^3)
Moisture content, %	52.59 (3)
Loss on Ignition, % Dry Weight Basis	25.80

The chemical analysis of the lime putty shows that the lime was produced from a dolomitic (magnesium containing) limestone (Table 16). The sulfur content is notable, as this implies that the lime putty may contribute sulfur to mortar mixes containing that material.

The thermal analysis results for the lime putty are shown in Figure 10. The major observations are:

- Endothermic reaction at 382°C with weight loss of about 5.2% and water evolution. This is consistent with the dehydration of magnesium hydroxide or $Mg(OH)_2$. This endotherm agrees with the chemical suggestion that the lime was made from dolomitic limestone.

- Major endothermic reaction at 493°C with a weight loss of 15.3% and water evolution. This endotherm is for the decomposition of portlandite or $Ca(OH)_2$.

[28] ASTM C109 specifies use of graded sand from compression tests.
[29] See http://www.virginialimeworks.com/tech/data/putty/TLPDatasheet.pdf.

- Endothermic peak at 741°C with weight loss of 5.3% and CO_2 evolution. This endotherm is consistent with the decomposition of calcite or $CaCO_3$. The weight loss implies a calcite content of 12%, a value exceeding the maximum of 7% provided in ASTM C1489.

Table 16: Chemical Analysis of Lime Putty

Chemistry (Oxidized Basis)		
Major Constituents		VLW - Wood Fired Lime Putty
Al_2O_3	%	0.50
SiO_2	%	3.63
Na_2O	%	<0.5
K_2O	%	0.07
MgO	%	17.11
CaO	%	77.02
TiO_2	%	0.04
MnO	%	0.02
Fe_2O_3	%	0.35
P_2O_5	%	<0.05
S	%	0.52
Sum of Major Constituents	%	99.26

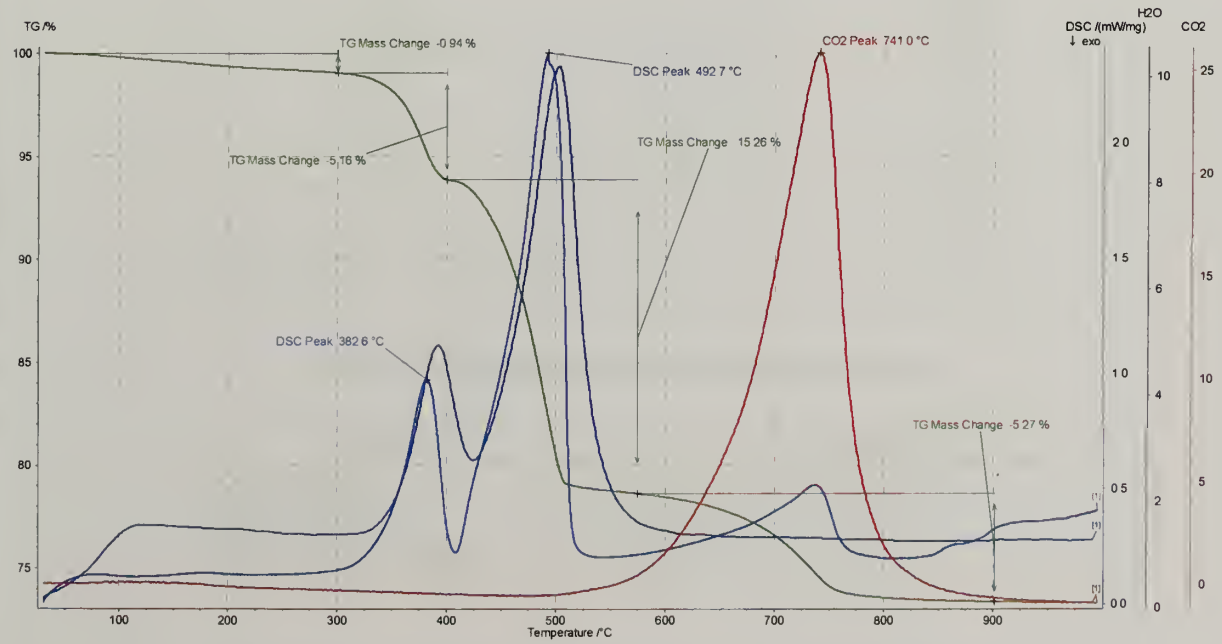

Figure 12: Simultaneous Thermal Analysis of Lime Putty

Dolomitic Lime (Graymont Type S)

Hydrated Type S dolomitic lime was obtained from the Graymont Lime Group[30]. This material is lime produced from calcination of dolomitic limestone followed by autoclave treatment to accomplish hydration. It is supplied as a dry powder packaged in polymer lined paper bags. It is produced to meet ASTM C206 and C207.

Characterization data is provided in Tables 17-19. The chemical analysis confirms that the limestone used in production of the lime was dolomitic (magnesium bearing). The packed bulk density of 40.4 lb./ft^3 agrees well with the value of 40 lb./ft^3 found in ASTM C1713.

Table 17: Loss on Ignition of Graymont Lime

LOI	26.32 %

Table 18: Chemical Analysis of Graymont Lime

Major Constituents		Graymont DoLime - Type S Hydrated
Al_2O_3	%	0.50
SiO_2	%	0.47
Na_2O	%	<0.5
K_2O	%	<0.01
MgO	%	39.45
CaO	%	58.31
TiO_2	%	<0.02
MnO	%	0.01
Fe_2O_3	%	0.19
P_2O_5	%	<0.05
S	%	0.39
Sum of Major Constituents	%	99.31

Table 19: Physical Data for Graymont Lime

Property	Average of 3
Loose density	0.44 g/cm^3 (27.73 lb./ft^3)
Packed density	0.65 g/cm^3 (40.40 lb./ft^3)
Specific surface area	13.584

[30] See http://www.graymont.com/prod_pressure_hydrate_S.shtml.

The thermal analysis of the Graymont lime is shown in Figure 13, and it is analogous to the data for the lime putty (Figure 13). The Graymont lime exhibits the following thermal events on heating:

- Endothermic peak at 394°C with a weight loss of 10.8% and water vapor evolution resulting from decomposition of $Mg(OH)_2$.
- Endothermic peak at about 440°C resulting from decomposition of portlandite or $Ca(OH)_2$.
- Endothermic peak at 514°C with a weight loss of 11.2% resulting from decomposition of $MgCO_3$.
- Endothermic peak at 779°C with a weight loss of 5.5% and CO_2 evolution resulting from decomposition of $CaCO_3$.

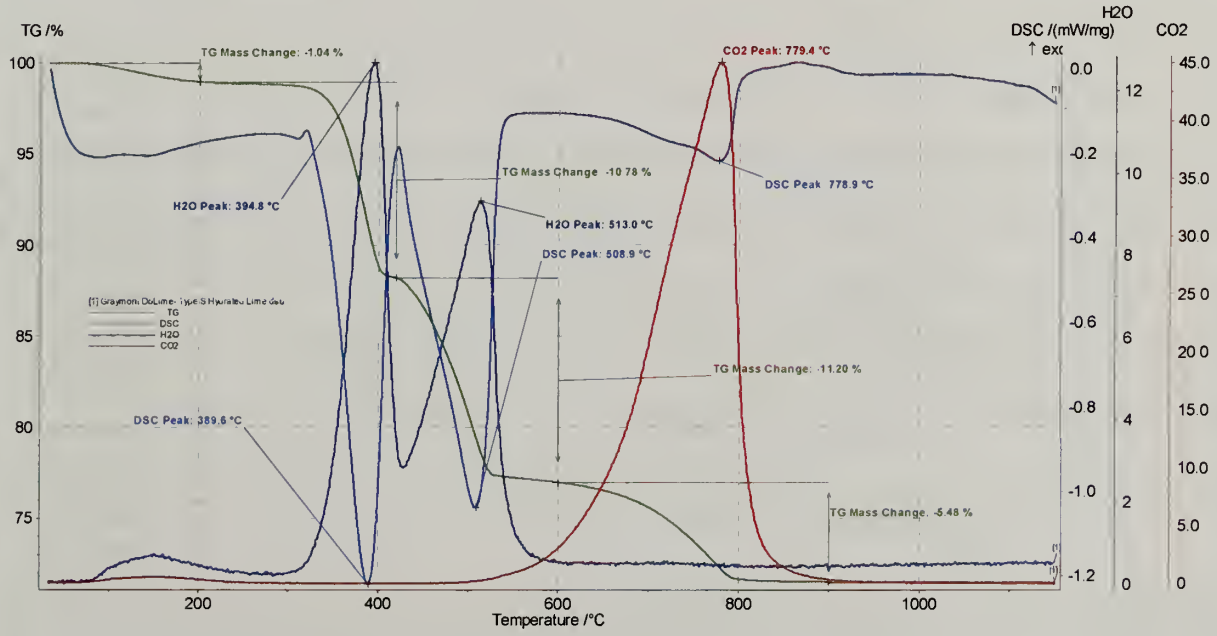

Figure 13: Simultaneous Thermal Analysis of Graymont Dolomitic Lime

great bag
nice sum error
use of 1738
send to John Wathne

Mortar Chemical Characterization and Physical Property Summary

Mortar Mix Goals and Compositions As-Made

The mortar mixes used in this research are given in Table 20 in volume and weight proportions. The weight proportions of mixes containing lime putty were adjusted so that the volumetric proportions on a dry weight basis would be achieved.

Table 20: Mortar Mixes Used in Research

	Comment	Relative Volume Rosendale Cement	Relative Volume Lime	Relative Volume Sand	Weight % Rosendale Cement	Weight % Lime Putty or Dolomitic Lime	Weight % Sand	Water Added	Pen. mm
C	ASTM C-10 Mix	1	0	0.65	50.0	0	50.0	26.2	2
1	Totten Type Mix	1	0	2¼	21.1	0	78.9	22.51	4
2	Low Lime (LP lime)	1	½	1½	26.4	12.6	61.0	16.57	2
3	High Lime (LP lime)	1	1	2	19.85	19.05	61.1	13.22	2
4	Low Lime (DL lime)	1	½	1½	28.25	6.37	65.37	24.77	4
5	High Lime (DL lime)	1	1	2	22.07	9.96	67.96	23.94	2
6	Manual Pointing (Mix 2)	1	½	1½	26.4	12.6	61.0	12.45	0.5
7	Grout Bag Pointing (Mix 2)	1	½	1½	26.4	12.6	61.0	17.5	3

Note: LP = lime putty, DL = dolomitic lime (High MgO lime), Sand = ASTM Graded Sand, Pen. = Vicat™ penetrometer (Penetration of wet mix in mm using a 12.44 mm diameter blunt penetrometer head of height 44.44 mm and weight 9.1 g). Volumes are expressed on a dry weight basis.

The methods in ASTM C1713 were used to verify that compositional goals were met with respect to cement content and volume proportions (Tables 20 and 21). The results show that all mixes made met the expected batch chemistry except for Mix 3. It appears that Mix 3 could have higher cement content than planned (Table 22).

The physical properties of the mortar show expected trends:

- The porosity increases as lime content increases.

good ★
Ca dissolution increases bad

- The porosity increases within the same mix as water content increases (Mixes 6, 2, and 7).

Table 21: Summary Data on Mortar Characterizations

Mix	CaO %	MgO %	Fe_2O_3 %	Calculated Cement %	Cement Goal %	BD g/cm^3	AP %	Fraction <1μ porosity
C	25.1	4.84	0.85	44.0	50.0	1.84	28.46	89.93
1	10.23	1.83	0.36	18.1	21.1	1.74	32.14	73.36
2	17.97	3.51	0.51	31.8	26.4	1.86	28.65	94.92
3	18.20	3.21	0.43	32.2	19.85	1.77	34.81	74.72
4	17.13	4.68	0.51	28.3	28.25	1.85	28.20	83.98
5	15.95	4.99	0.42	23.3	22.07	1.75	29.83	92.76
6	19.16	3.62	0.55	23.3	26.4	1.97	24.56	92.05
7	19.32	3.63	0.55	29.1	26.4	1.73	30.42	88.82

Table 22: Actual Mortar Composition in Volume Proportions

Mix	Goal Cement:Lime:Sand Volume	Actual Smooth Batch Proportions Volume
C	1:0:0.65	1:0:0.6
1	1:0:2¼	1:0:2
2	1:½:1½	1:½:1½
3	1:1:2	1:0.6:1.6
4	1:½:1½	1:½:1½
5	1:1:2	1:1:2
6	1:½:1½	1:½:1½
7	1:½:1½	1:½:1½

Degree of Carbonation

Rainbow pH indicator solution was applied to a cut surface of Mix 1 to determine the degree of carbonation of the specimens (Figure 14). The blue color indicates a basic pH due to the presence of hydrated lime (no carbonation) while the outer surface is yellow showing that the material is completely carbonated. Similar results were reported by Weiss and Schorck after accelerated laboratory curing[31].

[31] Norman Weiss and Jennifer Schork, *Rosendale and French Lime Mortars*, Presented at the American Historic Cement Conference, New York (2011).

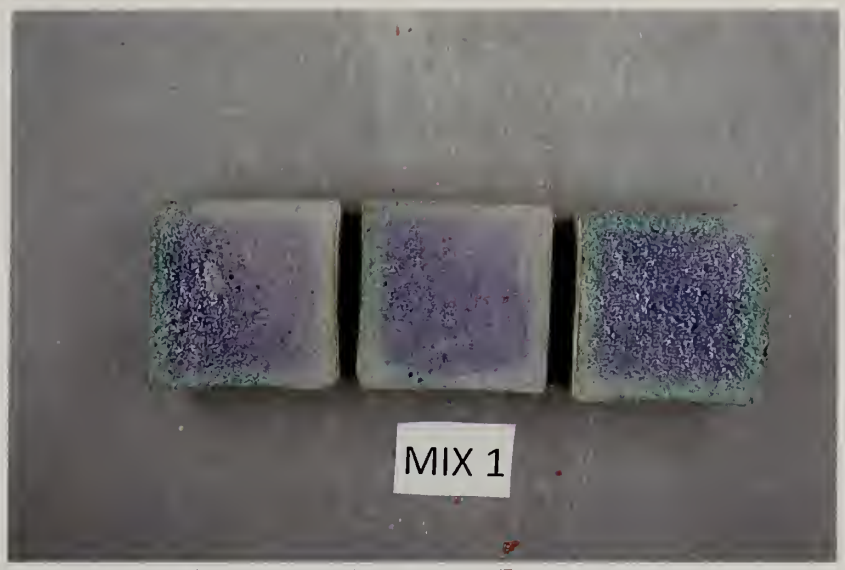

Figure 14: Rainbow pH Indicator Applied to Cut Faces of Cured Mortar Cubes (2" Side)

X-ray Diffraction Characterization of Mortars

The mineral phases in the mortar specimens as-cured were compared to phases reported in the literature and found in the cement characterization (above), with results presented in Table 23. The XRD traces and peak identifications of Mortars C, 1, and 2 are given in Figures 15-17.

Table 23: Summary of XRD Mineralogy Results for Rosendale Cement and All Mortars

Rosendale Cement (A & B)	Cement Phases Identified in STP 1494	All Mortars
Periclase (MgO)	Present	Present
Lime (CaO)		
Calcite ($CaCO_3$)	Present	Present
Spurrite [$Ca(SiO_4)2CO_3$]		
Anhydrite ($CaSO_4$)		
Portlandite [$Ca(OH)_2$]	Present	Present
Larnite (Ca2SiO4), aka belite	Present	Present
Quartz (SiO_2)	Present	Present
Muscovite $[(K,Na)(Al,Fe,Mg)(Si_{3.1}Al_{0.9})O_{10}(OH)_2]$		
		Calcio-olivine [$Ca_2(SiO_4)$]
		Merwinite ($3CaO \cdot MgO \cdot 2SiO_2$)
	Present	Gehlenite ($2CaO \cdot Al_2O_3 \cdot SiO_2$)
		Bassinite ($CaSO_4 \cdot 0.5H_2O$)
Amorphous phase (noted)	Present	Suggested

Figure 15: X-ray Diffraction Results for Mix C As-cured

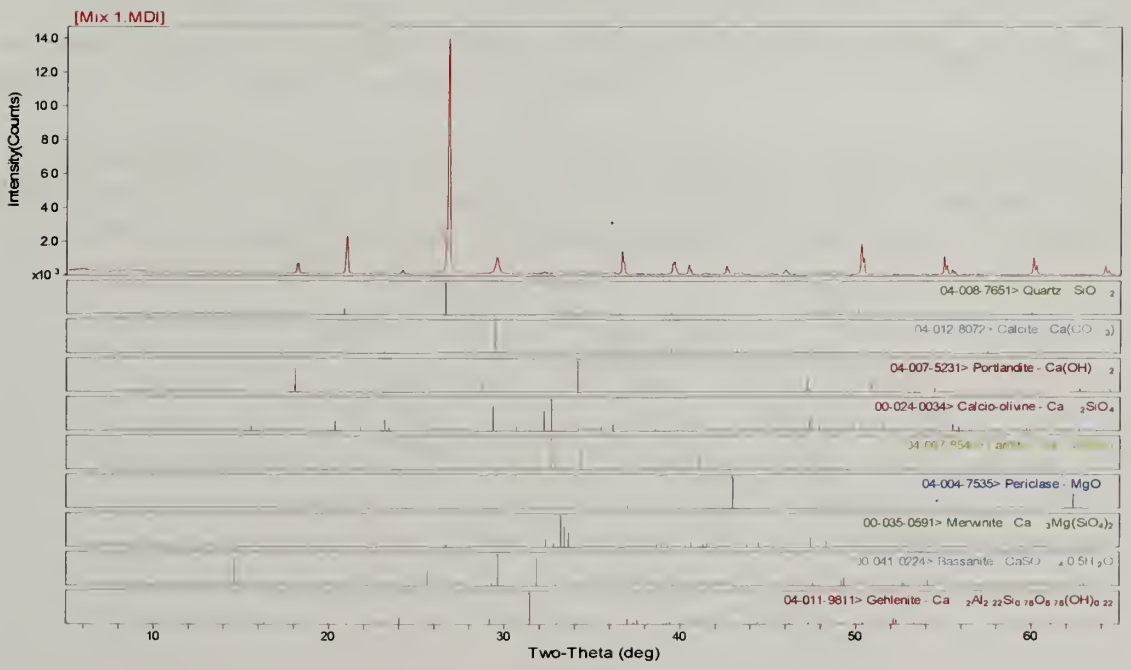

Figure 16: X-ray Diffraction Results for Mix 1 As-cured

Winston Hatbuc art thou
Frankendale - have mercy
the Knowledge - and power - of
the Found action - Flow
the Rosemarie guarrie

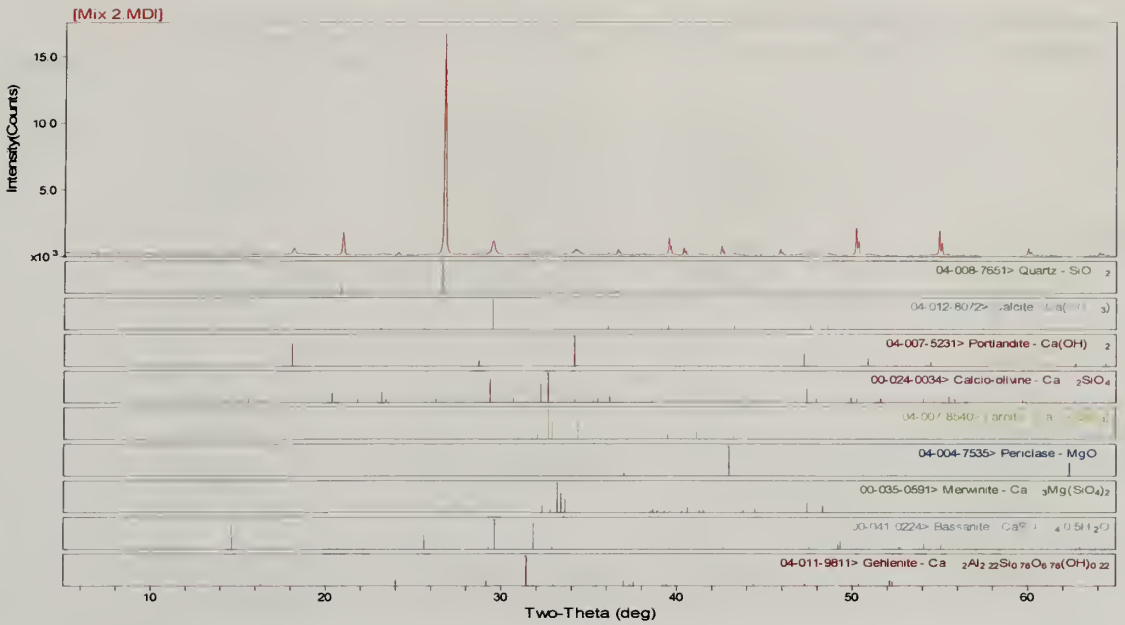

Figure 17: X-ray Diffraction Results for Mix 2 As-cured

Thermal Analysis Characterization

The thermal analysis results present a characterization of the materials on heating. The types of changes include endothermic reactions (usually indicating decomposition or melting) and exothermic reactions (indicating formation of a new mineral on heating). A review of thermal analysis in cementitious materials is available[32].

Thermal analysis results for Rosendale cements A and B (separate shipments) are given in Tables 24 and 25, with traces on heating given in Figures 18 and 19. The results suggest variations in the minor constituents of the two sequential shipments received for this research.

[32] V. S. Ramachandran, R. Paroli, J. Beaudoin, and A. Delgado, *Handbook of Thermal Analysis of Construction Materials*, Noyles (2003).

Table 24: Thermal Analysis Results for Rosendale Cement Specimen A
(Used in Preliminary Experiments)

Temperature, °C	Weight Change	Heat Flow	Evolved Gas	Reason
RT to 200°C	-0.14	Endothermic	H2O	
318	Negligible	Exothermic	Slight CO_2	
401	-0.57	Endothermic	H_2O	
575	None	Endothermic	None	Quartz inversion
~680	Not quantified	Endothermic	None	Suspected $MgCO_3$ decomposition
723	-2.10	Endothermic	CO_2	Calcite decomposition
~840	Slight	Encothermic	Slight CO_2 (SO_2 not monitored)	Carbonate and sulfate decomposition
~980	Negligible	Endothermic	None	Melting

Table 25: Thermal Analysis Results for Rosendale Cement Specimen B
(Used in all experiments reported in the results chapter).

Temperature, °C	Weight Change	Heat Flow	Evolved Gas	Reason
107	-0.22	Endothermic	H_2O	Drying and ettringite decomposition.
439	-0.80	Endothermic	Sl. CO_2	Ettringite and CSH phase decomposition.
815	-10.29 (Includes decomposition at 873C).	Endothermic	Major CO_2	Calcite decomposition.
873	About 2%	Endothermic	CO_2	Carbonate and sulfate decomposition
~980	Negligible	Endothermic	None	Slight melting

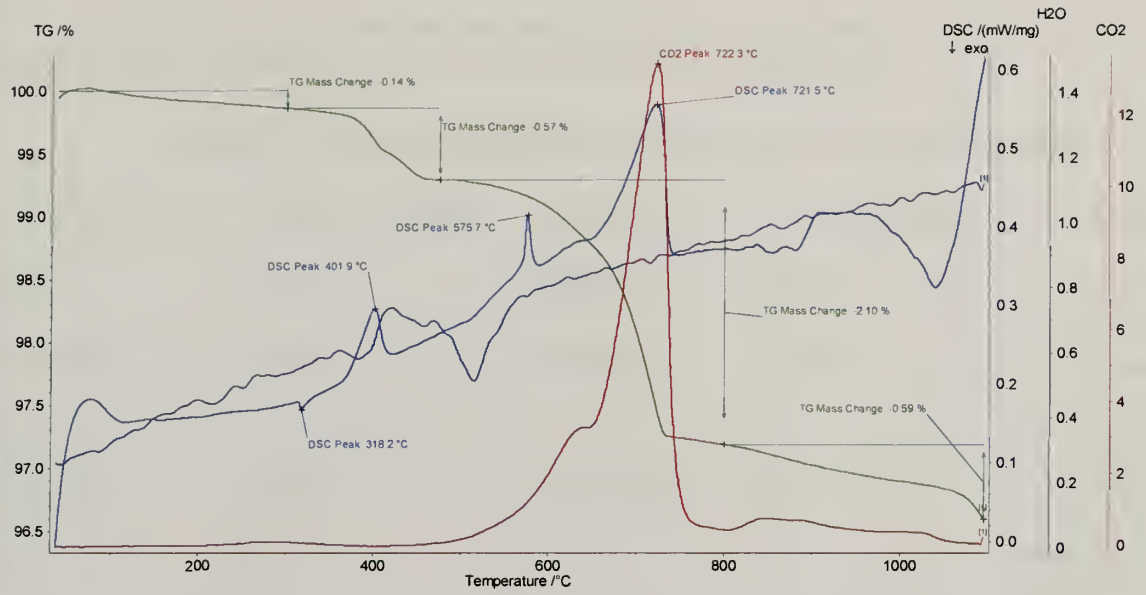

Figure 18: Thermal Analysis of Rosendale Cement Specimen A

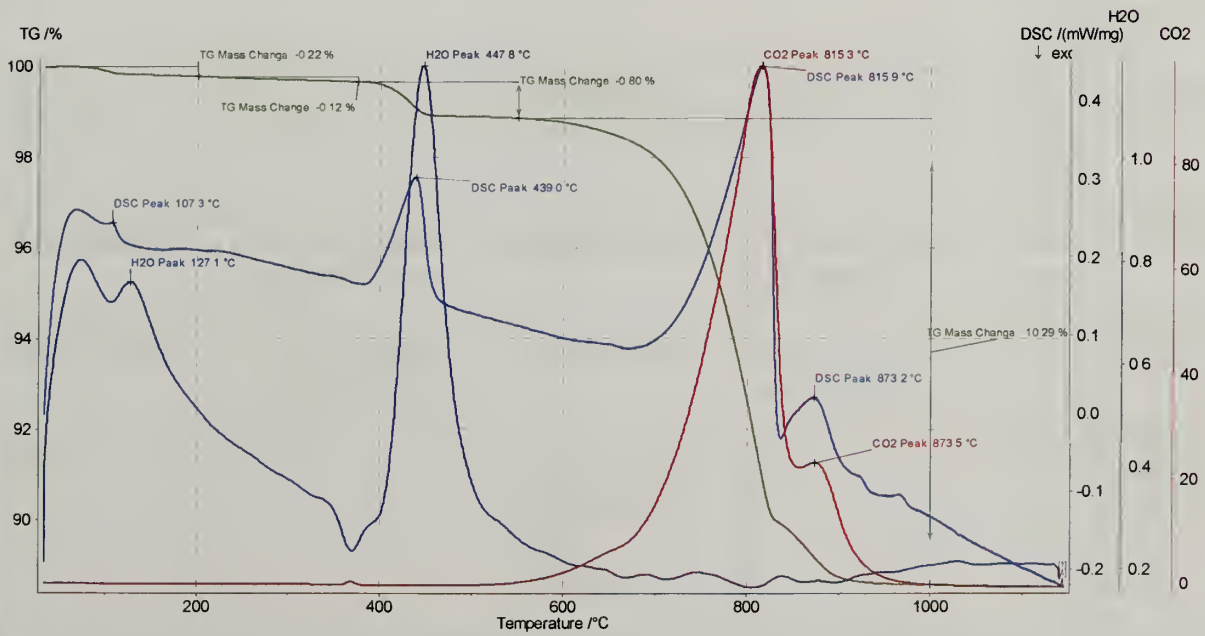

Figure 19: Thermal Analysis of Rosendale Cement Specimen B

A summary of STA results for hardened mortars is provided in Table 26. Individual thermal analysis graphs for the mortars are presented in Figures 20-27.

Table 26: Thermal Analysis Summary for Cured Mortar Specimens

Temperature, °C	Weight Change	Heat Flow	Evolved Gas	Reason[33]
100	-0.27	Endothermic	H_2O	Drying, ettringite decomposition.
180-190	-1.04	Endothermic	H_2O	Etrringite and cement hydrate decomposition
390-400	-2.16	Endothermic	$H_2O + CO_2$	Decomposition of tricalcium aluminate and/or calcium iron aluminates.
450-460	-0.9	Endothermic	H_2O	Dehydration of portlandite or $Ca(OH)_2$.
~575	0	Endothermic	None	Quartz inversion
680-780	-5.22	Endothermic	CO_2	Magnesite and calcite decomposition.
~847 (Note 1)	Total for peaks 800-900°C of -0.76	Endothermic	CO_2 (SO_2 not monitored)	Carbonate and sulfate decomposition
~887 (Note 1)	Total for peaks 800-900°C of -0.76	Endothermic	CO_2 (SO_2 not monitored)	Carbonate and sulfate decomposition
>900	NA	Slight exotherm followed by a larger endotherm.	NA	Initial surface reaction of lime and silica followed by melting.

Note 1: Decompositions between 800 and 900°C were seen in the Rosendale cement specimens. Similar decompositions were seen in hardened mortar specimens and especially in specimens containing either high calcium lime or dolomitic lime in their mixture (Note especially Mixes 5 and 7).

[33] See reference 5.

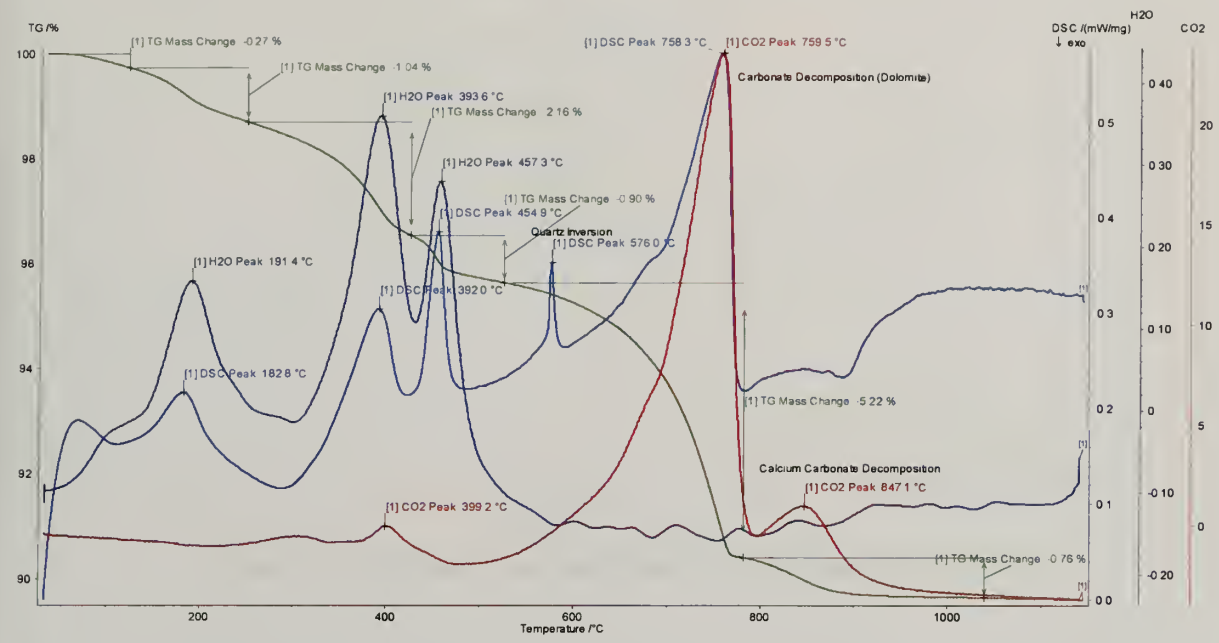
TG /%
DSC /(mW/mg)
↓ exo
H2O
CO2
[1] TG Mass Change -0.27 %
[1] TG Mass Change -1.04 %
[1] H2O Peak 393.6 °C
[1] TG Mass Change -2.16 %
[1] H2O Peak 457.3 °C
[1] TG Mass Change -0.90 %
[1] DSC Peak 454.9 °C
Quartz Inversion
[1] DSC Peak 576.0 °C
[1] H2O Peak 191.4 °C
[1] DSC Peak 392.0 °C
[1] DSC Peak 182.8 °C
[1] DSC Peak 758.3 °C
[1] CO2 Peak 759.5 °C
Carbonate Decomposition (Dolomite)
[1] TG Mass Change -5.22 %
Calcium Carbonate Decomposition
[1] CO2 Peak 847.1 °C
[1] CO2 Peak 399.2 °C
[1] TG Mass Change -0.76 %
Temperature /°C

Figure 20: Thermal Analysis Results for Mortar C As-cured

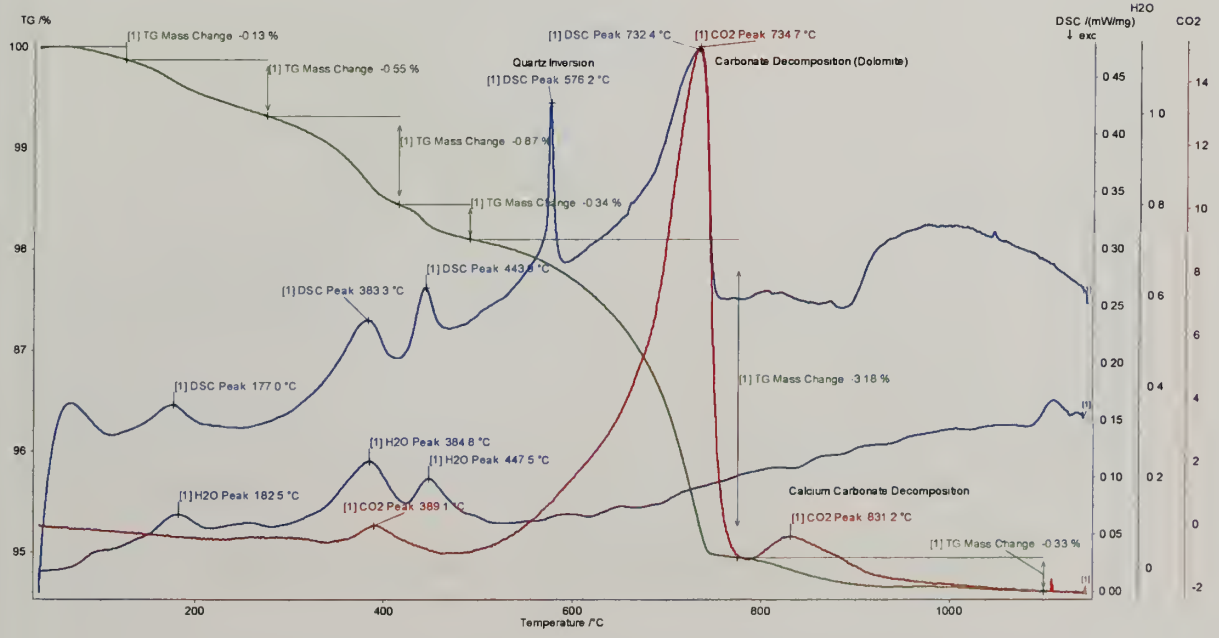
TG /%
DSC /(mW/mg)
↓ exo
H2O
CO2
[1] TG Mass Change -0.13 %
[1] TG Mass Change -0.55 %
[1] DSC Peak 732.4 °C
[1] CO2 Peak 734.7 °C
Quartz Inversion
[1] DSC Peak 576.2 °C
Carbonate Decomposition (Dolomite)
[1] TG Mass Change -0.87 %
[1] TG Mass Change -0.34 %
[1] DSC Peak 443.5 °C
[1] DSC Peak 383.3 °C
[1] DSC Peak 177.0 °C
[1] TG Mass Change -3.18 %
[1] H2O Peak 384.8 °C
[1] H2O Peak 447.5 °C
[1] H2O Peak 182.5 °C
[1] CO2 Peak 389.1 °C
Calcium Carbonate Decomposition
[1] CO2 Peak 831.2 °C
[1] TG Mass Change -0.33 %
Temperature /°C

Figure 21: Thermal Analysis Results for Mortar 1 As-cured

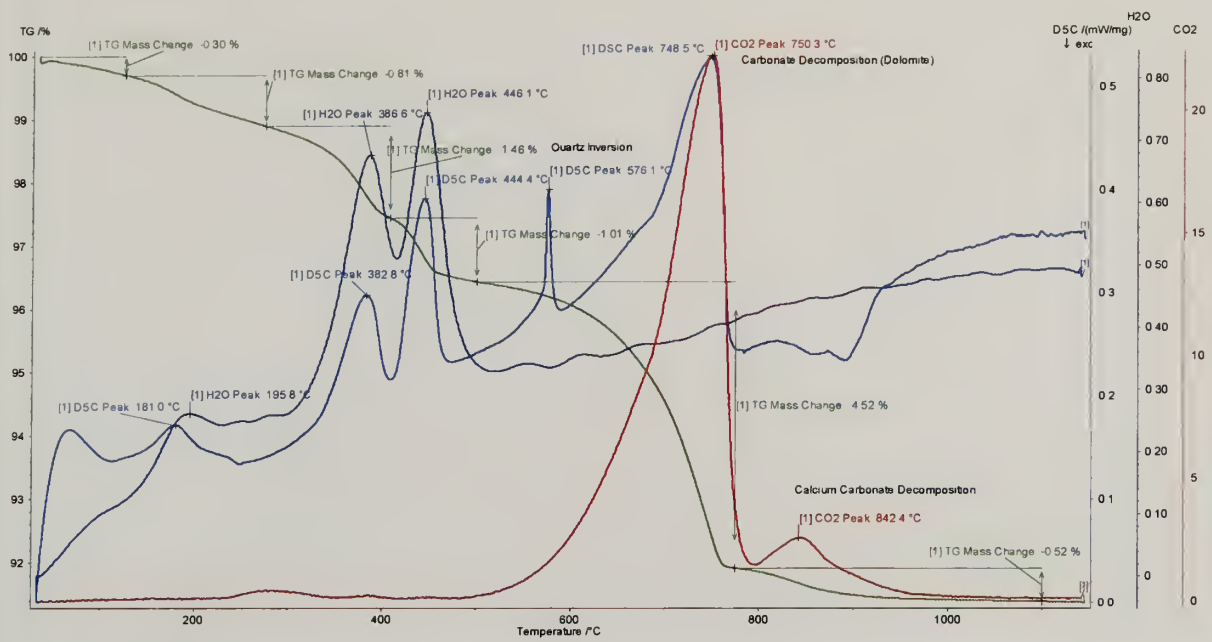
TG /%
H2O
D5C /(mW/mg)
↓ exo
CO2
[1] TG Mass Change -0.30 %
[1] TG Mass Change -0.81 %
[1] H2O Peak 386.6 °C
[1] H2O Peak 446.1 °C
[1] DSC Peak 748.5 °C
[1] CO2 Peak 750.3 °C
Carbonate Decomposition (Dolomite)
[1] TG Mass Change -1.46 %
Quartz Inversion
[1] D5C Peak 444.4 °C
[1] D5C Peak 576.1 °C
[1] TG Mass Change -1.01 %
[1] D5C Peak 382.8 °C
[1] D5C Peak 181.0 °C
[1] H2O Peak 195.8 °C
[1] TG Mass Change -4.52 %
Calcium Carbonate Decomposition
[1] CO2 Peak 842.4 °C
[1] TG Mass Change -0.52 %
Temperature /°C

Figure 22: Thermal Analysis Results for Mortar 2 As-cured

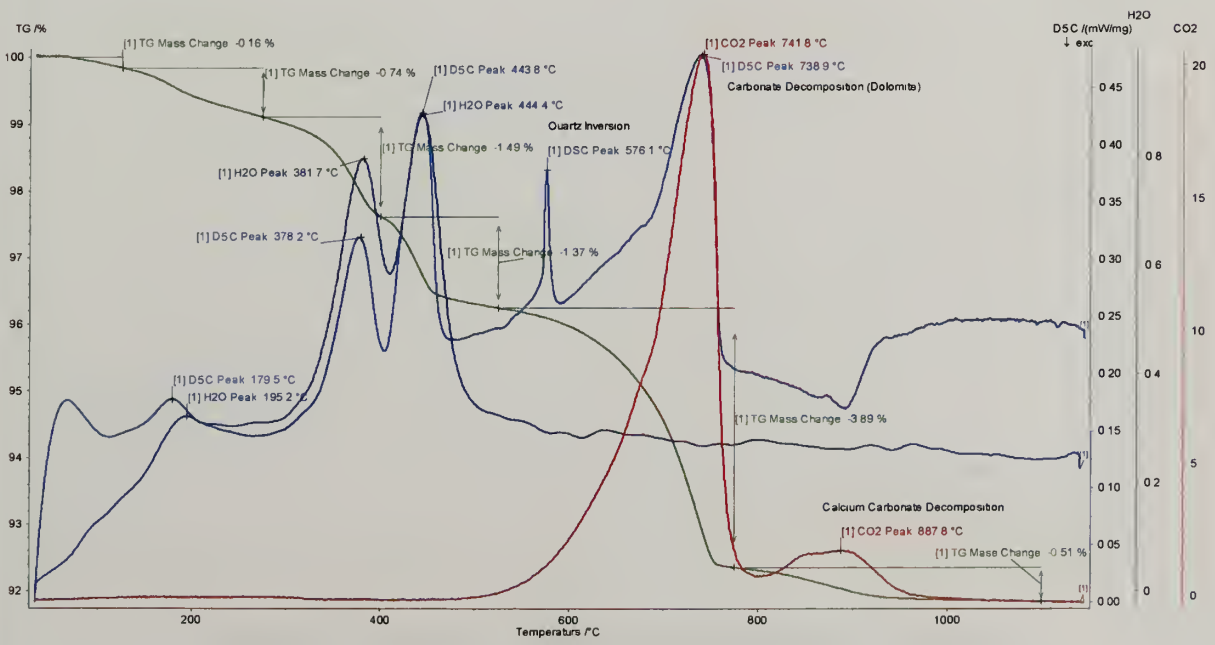
TG /%
H2O
D5C /(mW/mg)
↓ exo
CO2
[1] TG Mass Change -0.16 %
[1] TG Mass Change -0.74 %
[1] D5C Peak 443.8 °C
[1] H2O Peak 444.4 °C
[1] CO2 Peak 741.8 °C
[1] D5C Peak 738.9 °C
Carbonate Decomposition (Dolomite)
Quartz Inversion
[1] TG Mass Change -1.49 %
[1] DSC Peak 576.1 °C
[1] H2O Peak 381.7 °C
[1] D5C Peak 378.2 °C
[1] TG Mass Change -1.37 %
[1] D5C Peak 179.5 °C
[1] H2O Peak 195.2 °C
[1] TG Mass Change -3.89 %
Calcium Carbonate Decomposition
[1] CO2 Peak 887.8 °C
[1] TG Mass Change -0.51 %
Temperature /°C

Figure 23: Thermal Analysis Results for Mortar 3 As-cured

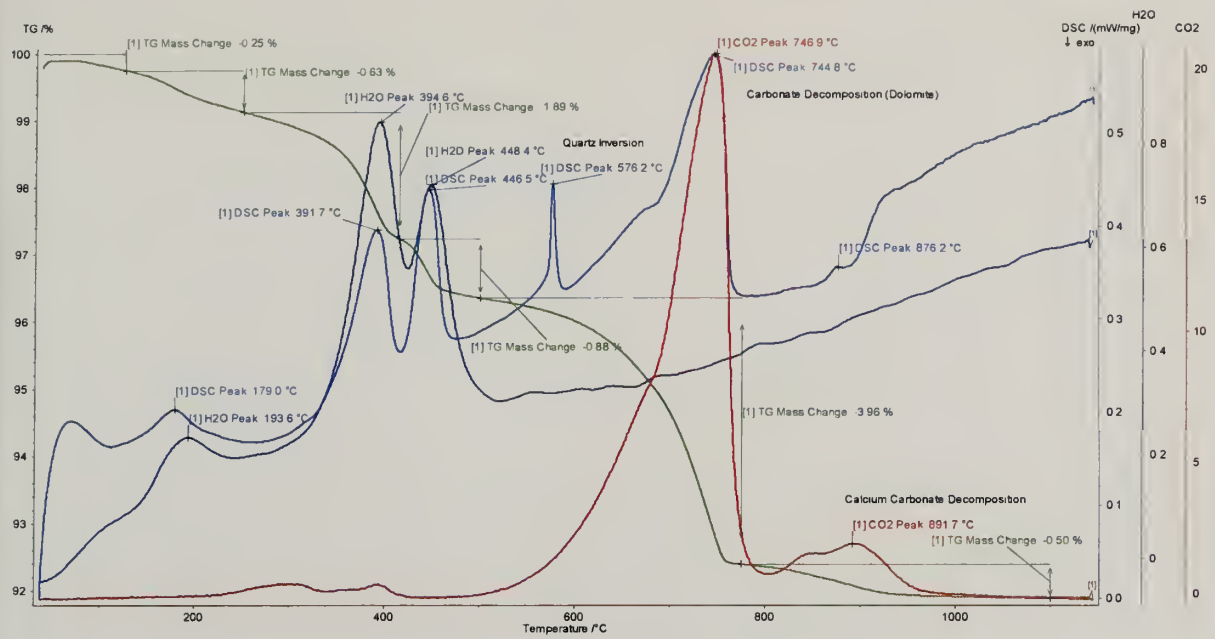
TG /%
DSC /(mW/mg)
↓ exo
H2O
CO2
[1] TG Mass Change -0 25 %
[1] TG Mass Change -0 63 %
[1] H2O Peak 394 6 °C
[1] TG Mass Change 1 89 %
[1] H2D Peak 448 4 °C
[1] DSC Peak 446 5 °C
Quartz Inversion
[1] DSC Peak 576 2 °C
[1] CO2 Peak 746 9 °C
[1] DSC Peak 744 8 °C
Carbonate Decomposition (Dolomite)
[1] DSC Peak 391 7 °C
[1] DSC Peak 876 2 °C
[1] TG Mass Change -0 88 %
[1] DSC Peak 179 0 °C
[1] H2O Peak 193 6 °C
[1] TG Mass Change -3 96 %
Calcium Carbonate Decomposition
[1] CO2 Peak 891 7 °C
[1] TG Mass Change -0 50 %
Temperature /°C

Figure 24: Thermal Analysis Results for Mortar 4 As-cured

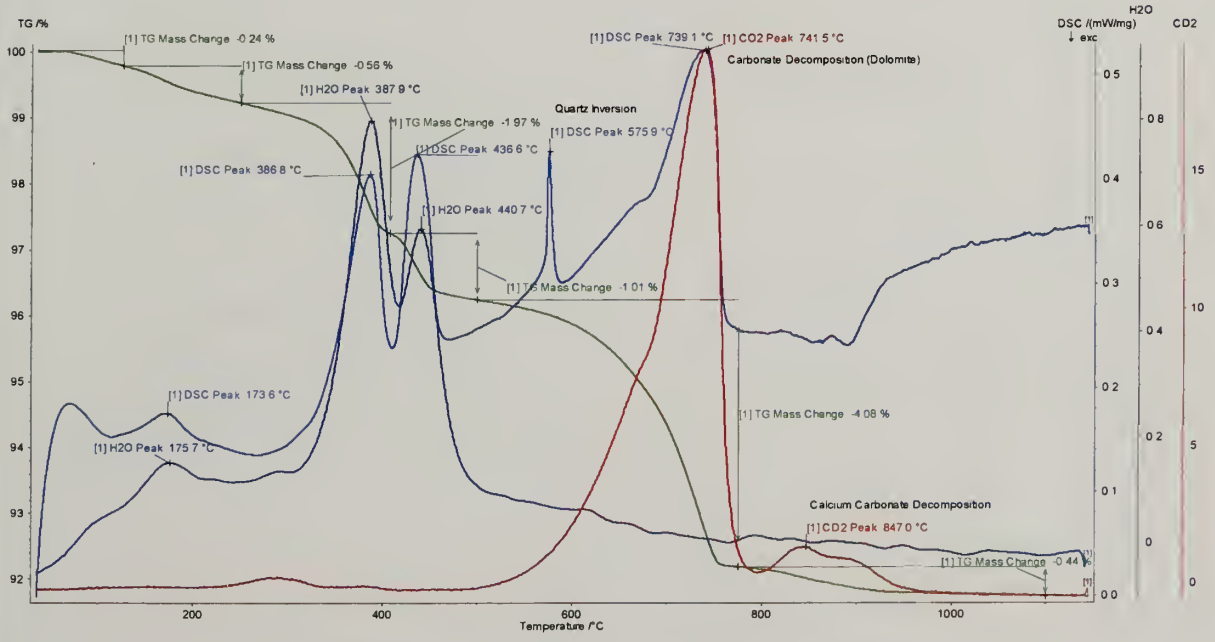
TG /%
DSC /(mW/mg)
↓ exo
H2O
CD2
[1] TG Mass Change -0 24 %
[1] TG Mass Change -0 56 %
[1] H2O Peak 387 9 °C
[1] TG Mass Change -1 97 %
[1] DSC Peak 436 6 °C
Quartz Inversion
[1] DSC Peak 575 9 °C
[1] DSC Peak 739 1 °C
[1] CO2 Peak 741 5 °C
Carbonate Decomposition (Dolomite)
[1] DSC Peak 386 8 °C
[1] H2O Peak 440 7 °C
[1] TG Mass Change -1 01 %
[1] DSC Peak 173 6 °C
[1] H2O Peak 175 7 °C
[1] TG Mass Change -4 08 %
Calcium Carbonate Decomposition
[1] CD2 Peak 847 0 °C
[1] TG Mass Change -0 44 %
Temperature /°C

Figure 25: Thermal Analysis Results for Mortar 5 As-cured

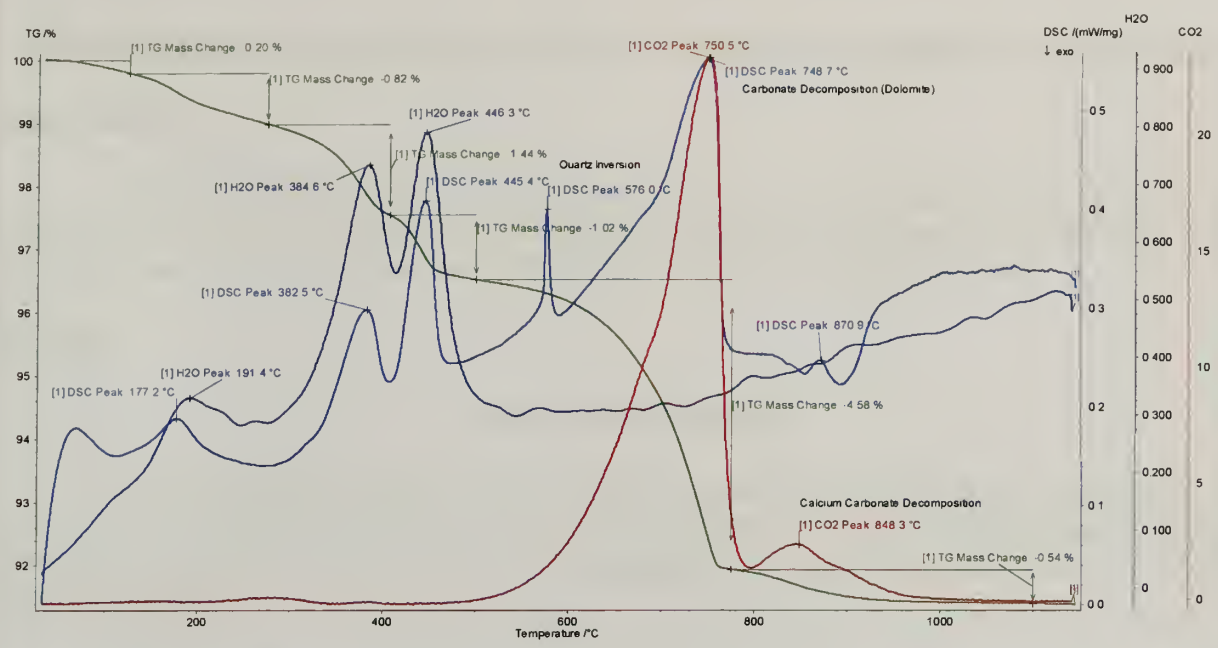
TG /%
DSC /(mW/mg)
↓ exo
H2O
CO2
[1] TG Mass Change 0 20 %
[1] TG Mass Change -0 82 %
[1] H2O Peak 446 3 °C
[1] TG Mass Change 1 44 %
[1] H2O Peak 384 6 °C
[1] DSC Peak 445 4 °C
Quartz Inversion
[1] DSC Peak 576 0 °C
[1] TG Mass Change -1 02 %
[1] CO2 Peak 750 5 °C
[1] DSC Peak 748 7 °C
Carbonate Decomposition (Dolomite)
[1] DSC Peak 382 5 °C
[1] DSC Peak 870 9 °C
[1] H2O Peak 191 4 °C
[1] DSC Peak 177 2 °C
[1] TG Mass Change -4 58 %
Calcium Carbonate Decomposition
[1] CO2 Peak 848 3 °C
[1] TG Mass Change -0 54 %
Temperature /°C

Figure 26: Thermal Analysis Results for Mortar 6 As-cured

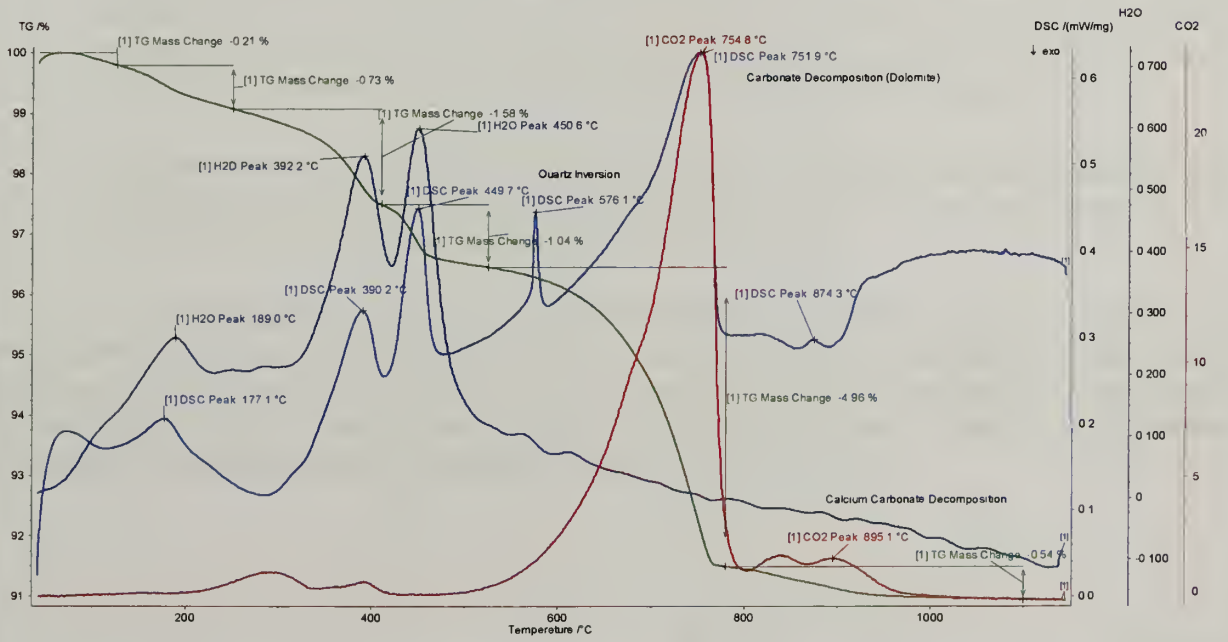
TG /%
DSC /(mW/mg)
↓ exo
H2O
CO2
[1] TG Mass Change -0 21 %
[1] TG Mass Change -0 73 %
[1] TG Mass Change -1 58 %
[1] H2O Peak 450 6 °C
[1] H2O Peak 392 2 °C
Quartz Inversion
[1] DSC Peak 449 7 °C
[1] DSC Peak 576 1 °C
[1] TG Mass Change -1 04 %
[1] CO2 Peak 754 8 °C
[1] DSC Peak 751 9 °C
Carbonate Decomposition (Dolomite)
[1] DSC Peak 390 2 °C
[1] DSC Peak 874 3 °C
[1] H2O Peak 189 0 °C
[1] DSC Peak 177 1 °C
[1] TG Mass Change -4 96 %
Calcium Carbonate Decomposition
[1] CO2 Peak 895 1 °C
[1] TG Mass Change -0 54 %
Temperature /°C

Figure 27: Thermal Analysis Results for Mortar 7 As-cured

Mechanical Properties and Water Vapor Transmission of Mortars

Introduction

The determination of mechanical properties and water vapor transmission of the mortar specimens fabricated in this study was for the purpose of characterization of the materials, so that the significance of the sea water immersion studies could be judged by the reader.

Strength

Compressive Strength

The compressive strengths of the mortars as-cured were determined according to the testing procedure in ASTM C109 (Table 27 and Figure 28). All mortars exhibit a gain in strength with time as expected. The significance of the magnitude of strength must be viewed in light of published criteria:

- ASTM C10 qualifies natural cement under the Standard with a minimum compressive strengths of 510 lb./in^2 (7-days) and 1020 lb./in^2 (28-days) are attained for mixes of 50% cement and 50% sand (as in mix C), with the sand specified as 20-30 as given in Specification C778, i.e. sand sized as finer than 20 mesh and coarser than 30 mesh in size (Note that C109 specifies use of "Graded Sand" in mortar compositions).

- Published values for Rosendale cement available in literature or from suppliers. Data represented as "typical" when tested according to ASTM C10 are an average of 1070 lb./in^2 (7-days) and an average of 2930 lb./in^2 (28-days)[34].

All mortars made in this study used "Graded Sand" meeting criteria in ASTM C778 rather than the coarser "20-30" sand as graded sand more closely resembles the size of sand particles in historic mortars at FSNM. It is well known that coarser gradations of aggregate in mortars provide higher strength values. Therefore, the strength values in Table 27 are considered as acceptable considering the sand gradation used in the compositions.

what is important about comp=tion results

[34] Personal Communication Michael P. Edison, Edison Coatings, to Denis Brosnan of January 3, 2012.

Table 27: Compressive Strength of Mortar Specimens as a Function of Curing Time

Mix	Cement to Lime to Sand By Volume	7-Day Compressive Strength lb./in^2	14-Day Compressive Strength lb./in^2	21-Day Compressive Strength lb./in^2	28-Day Compressive Strength [lb./in^2
C	1:0:0.65	495.2	728.5	819.0	768.4
1	1:0:2¼	NA	141.0	209.1	197.0
2	1:½:1½	98.7	359.1	384.0	563.8
3	1:1:2	NA	269.2	348.9	471.9
4	1:½:1½	112.9	436.2	410.5	516.1
5	1:1:2	115.9	427.0	490.8	381.5
6	1:½:1½	134.8	571.5	704.6	628.7
7	1:½:1½	112.6	427.3	433.5	481.6

Figure 28: Cube Compression Test

Tensile Strength

The tensile strength of the mortars was measured using the diametral compression method given in ASTM D3976. In this method, a cylindrical specimen is tested on edge such that a tensile failure is seen (Figures 29-31). The test is commonly called either "tensile splitting" or the "Brazilian test", the latter because it was developed to measure the strength of Brazil nuts. A typical tensile failure will result in the specimen splitting into halves with a relatively smooth fracture surface with the crack oriented in a vertical direction (Figures 30 and 31).

Figure 29: Diametral Compression Test Configuration (Image 2039)

Figure 30: Close Up of Specimen After Failure (Image 2042)

Figure 31: Failed Specimens after the Test (Image 2043)

Tensile strengths of 28-day cured mortars are provided in Table 28. Weiss and Schork[35] found that Type O masonry mortars exhibited tensile strengths of 188-333 lb./in^2, and mortars with natural hydraulic lime and sand exhibited tensile strengths less than about 72 lb./in^2 (data

[35] Norman Weiss and Jennifer Schork, *Rosendale and French Lime Mortars*, Presentation – The American Historic Cement Conference, New York (2011).

on Rosendale cement and sand was not presented). The values in Table 28 are values that might be expected based in the data of Weiss and Schork.

Table 28: Tensile Strengths of Mortars after 28 Days

Mix	Number	Length [inches]	Diameter [inches]	Max applied load [lb_f]	Tensile strength, $lb./in^2$	
C	1	2.002	3.964	1085	87.0386	
	2	2.0095	3.9805	1688	134.3	**Average** $lb./in^2$
	3	2.0045	3.966	1566	125.4	115.6
1	1	2.006	3.926	729	58.92	
	2	2.0085	3.9355	589	47.43	
	3	2.009	3.895	565	45.96	50.8
2	1	1.9975	3.932	616	49.92	
	2	1.9965	3.996	435	34.71	
	3	2.0205	3.966	558	44.33	43.0
3	1	1.9925	3.9545	591	47.75	
	2	2.0015	3.9335	982	79.40	
	3	1.9895	3.962	961	77.61	68.2
4	1	1.998	3.948	557	44.95	
	2	1.9985	3.952	639	51.50	
	3	2.0035	3.97	738	59.06	51.8
5	1	2.001	3.945	663	53.46	
	2	1.999	3.935	816	66.04	
	3	2.0065	3.934	729	58.79	59.4
6	1	2.0045	3.968	547	43.78	
	2	2.0105	3.9905	534	42.37	
	3	2.0035	3.9535	573	46.05	44.1
7	1	2.0045	3.9535	850	68.28	
	2	2.0065	3.958	767	61.48	
	3	BROKEN				64.9

Modulus of Elasticity of Mortars

The modulus of elasticity (MOE) for as-cured mortar cubes was measured during loading in compression with simultaneous recording of load and deflection. The load values were converted to stress with the deflection converted to strain, and the modulus of elasticity (stress/strain) was computed. Sonic measurements of MOE were not possible with a small specimen set because of variability in sonic response with the 2" cubes of this study[36].

The "mechanical" measurement in compression essentially mimics the way that such measurements were obtained prior to the development of ultrasonic measurements[37]. The mechanical measurement of MOE in compression is provided in ASTM C469. Using mechanical methods, Carlton found natural cement and sand mortar compositions to provide MOE values in the approximate range of 1,250,000 lb./in^2 to 1,360,000 lb./in^2 with portland cement mortars providing MOE values of about 1,950,000 lb./in^2 to 2,500,000 lb./in^2. This data supports that the fact that portland cement mortars are "stiffer" than natural cement mortars, as the portland cement mortars have higher MOE values.

The stress-strain diagram for Mortar C is shown in Figure 32 where a linear regression analysis was found to determine the slope of the line over the range of loading of the specimen, where the slope is the Modulus of Elasticity value (coefficient of x). The data shows an initial higher slope (arrow) followed by a more uniform lower slope, i.e. there is a difference in initial MOE and average MOE, the latter obtained from the range of loading prior to failure. Some investigators might link the initial material response to a period of "crack initiation" and the continued response as due to a period of "crack propagation".

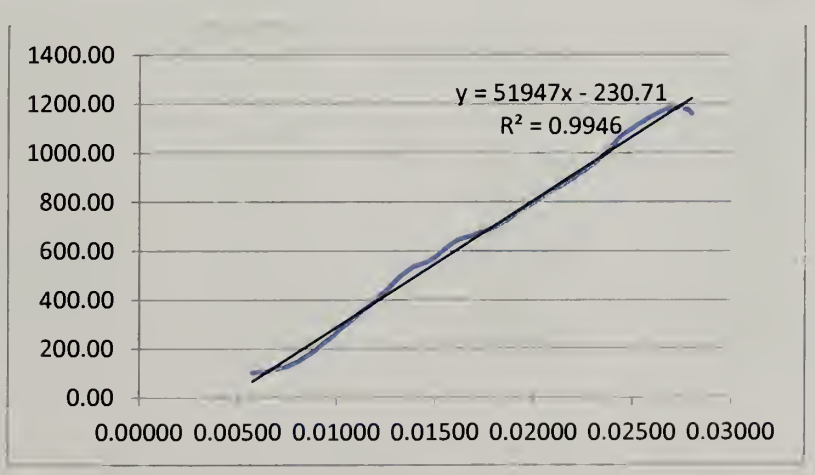

Figure 32: Stress-Strain Diagram for Mortar C
(Vertical axis Stress in lb./in^2 and horizontal axis strain in in./in.)

[36] ASTM C215, *Standard Test Method for Fundamental Transverse, Longitudinal, and Torsional Resonant Frequencies of Concrete Specimens.*

[37] Louis Carlton, *Cement and Concrete*, McGraw Publishing Company (1907). Available on *Google Books*.

The data is shown in Table 29 for the as-cured mortar specimens of this project. Several observations are:

- The initial MOE values for the mortars are comparable to those reported by Carlton (Reference 4) in 1907. It is likely that Carlton could only measure deflection in the initial stage of compression using mechanical gauges, so his reported values are likely from initial deformations.

- The regression values are lower than initial values, but due to a larger data accumulation range that likely represent differences between mixes. For example, the strength of Mortar C is greater than that of Mortar 1 (Table 1 and σ_{max}) reflecting the higher cement content of Mix C, but this trend is not obeyed in the initial MOE values.

- Since the values in Table 3 or for individual specimens (rather than averages), only limited analysis is possible. The best comparisons may be Mixes C and 1 (discussed above) and Mixes 6, 2, and 7, the latter with the same batch proportions but differences in water content. Mix 6 has the highest strength of maximum stress and the highest MOE of the three with lowest water content in fabrication, while the MOE and strength related data are about the same (considering scatter expected in data).

Table 29: Maximum Stress and MOE Data from Statistical Analysis (Individual Measurements)

Mortar	σ_{max} Maximum Stress in Compression	MOE_{max} Initial MOE	$MOE_{regression}$ Regression Fit of Slope
C	1187	1,473,338	51,112
1	465	2,892,950	24,546
2	676	NA	56,300
3	684	1,232,277	48,230
4	643	NA	49,449
5	854	2,110,733	82,055
6	1213	NA	86,631
7	951	3,436,206	69,836

Water Vapor Transmission

Water vapor transmission (WVT) of 28-day cured mortar specimens was measured using the "open cup" procedure in ASTM E96. The average laboratory conditions (for evaporation from the specimens) were as follows:

Average Temperature:	12.1°C (53.8°F)
Average Relative Humidity:	70.5%

A typical experimental curve for Mix C with the open cup method is shown in Figure 33. The evaporation rate is linear with one plot for each of the three specimens, and the slope of each line (the coefficient of x) is the evaporation rate. The values were averaged, and the water vapor transmissions were calculated using the exposed areas of the specimens (Table 30).

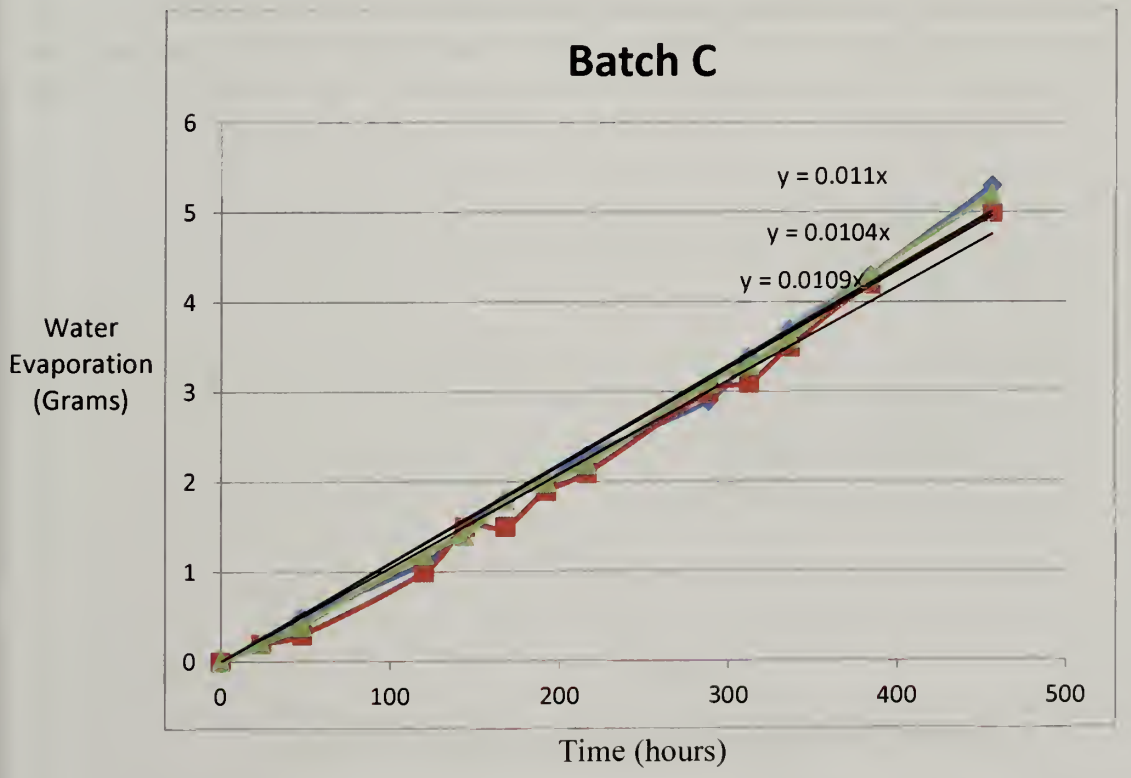

Figure 33: Water Evaporation Rate for Mix C

Table 30: Water Vapor Transmission (WVT) in 28 Day Cured Mortar Specimens

Mix	Goal	Bulk Density g/cm^3	Apparent Porosity %	Percentage <1μ porosity	Average WVT g/m^2-hr.
C	1:0:0.65	1.84	28.46	89.93	4.16
1	1:0:2¼	1.74	32.14	73.36	6.89
2	1:½:1½	1.86	28.65	94.92	5.33
3	1:1:2	1.77	34.81	74.72	5.34
4	1:½:1½	1.85	28.20	83.98	5.77
5	1:1:2	1.75	29.83	92.76	4.85
6	1:½:1½	1.97	24.56	92.05	4.04
7	1:½:1½	1.73	30.42	88.82	5.73

The data in Table 30 suggests that the WVT Rosedale-sand mixtures were sensitive to batch proportions with higher sand content providing higher WVT values. In mixes containing lime, the lime content did not seem to affect WVT. It is, however, clear that mix porosity (as influenced by increasing water content) had a strong influence on WVT (Figure 34).

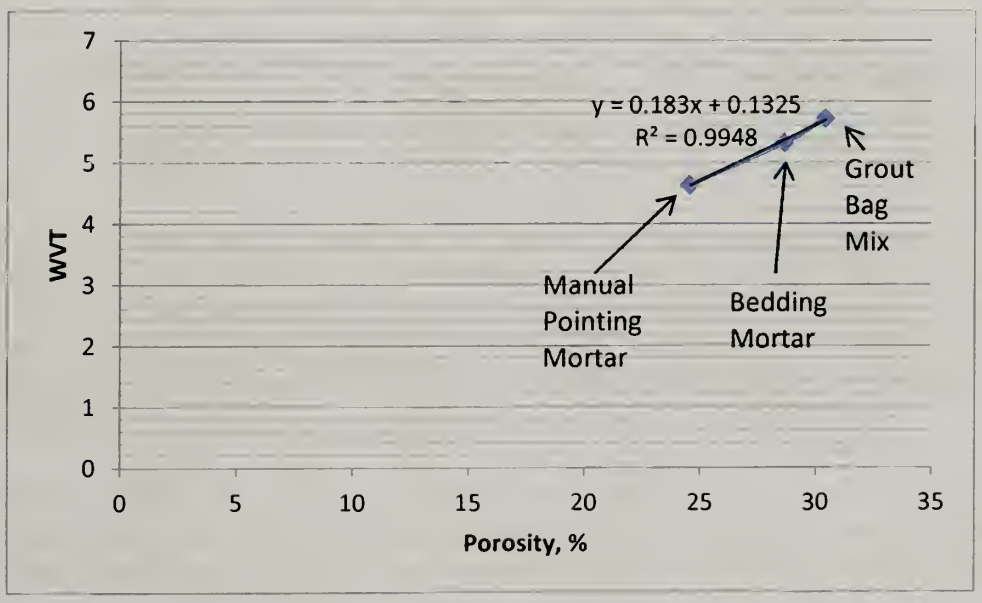

Figure 34: Water Vapor Transmission for 1:½:1½ Mixes

Using the same procedure, Weiss and Schork (reference 2) reported the following values: Lime, 4.94 g/m^2-hr.; Type O masonry mortar or 1:2:9, 2.4-3.4 g/m^2-hr.; Type N masonry mortar or 1:1:6, 1.76-2.25 g/m^2-hr.; natural hydraulic lime NHL 5, 3.8 g/m^2-hr.; and natural hydraulic lime NHL 2 of 4.3 g/m^2-hr.

The important observation from this work for restoration is that all Rosendale mixes exhibit slightly greater water vapor transmission than the portland cement mortars Types N and O as reported by Weiss and Schork. Thus, Rosendale mortars for restoration, depending on formulation and sand sizing, may provide more capacity for masonry to dry out.

other brew details
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different ones
remaining, and possible

-OH

-NH2

What about acid

Chemical Interaction with Sea Water

Cured mortar cubes were immersed in simulated sea water for various dwell periods allowing for the sea water to remove or add atomic species to the cubes by solution or absorption respectively, thus forming an altered immersion fluid called the "leachate". The analysis of leachate solutions from various compositions allowed for the following comparisons on sea water interaction with the mortars:

1. Effect of *cement content* in mortars without lime addition, Mixes C and 1.
2. Effect of *high calcium lime (HC) level*, Mixes 2 and 3.
3. Effect of *dolomitic lime (DL) level*, Mixes 4 and 5.
4. Effect of *density* at constant composition, Mixes 4, 6, and 7.

There was disagreement in absolute concentration values between ICP[38] data and IC[39] data for leachate solutions. The calcium solution data from IC and ICP analyses for one leachate solution are compared in Table 31.The magnitude of data points is similar, but the data reflects experimental variation when comparing the analytical techniques.

Table 31: Comparison of IC and ICP Data for Calcium

Soaking Period	IC Analysis (μg/g)	ICP Analysis (μg/g)
7-days	1908	1370
28-days	1849	1586

It is well known that IC analyses are subject to interferences. The interferences are particularly applicable to analyses involving simultaneous detection of calcium and magnesium. For this reason, ICP data was used for cations (sodium, potassium, calcium, and magnesium), while IC data was used for anions (chloride and sulfate). Another possible source of errors was the dilutions required to alter leachate solutions so they were within the detection limits of the IC and ICP instruments.

Selected mortar cubes were immersed on dilute hydrochloric acid solution (0.5% HCl) for seven days to demonstrate the difference between dilute acid and sea water on leaching. The acid data is important in restoration because muriatic acid (HCl) is used in masonry cleaning.

Cement-Sand Mortars

The cement-sand mortar specimens were found to release atomic species as ions into salt water solution including sodium, potassium, and calcium while absorbing or "up taking" other atomic species including sulfate and chloride. The release of calcium (Ca) from mortars Mix C and Mix 1 as a function of time are shown in Figure 35. The higher cement content Mix C (50% cement by weight) exhibits an initial release of calcium and the solution exhibits a parabolic relationship with time. By contrast, the quantity of calcium released from Mix 1 (21.1% cement)

[38] ICP refers to an analysis using inductively coupled plasma via atomic absorption techniques.
[39] IC refers to an analysis using ion chromatography.

releases more calcium to the solution, and the release is also parabolic. The parabolic relationship between release of calcium and time suggests that the rate of solution is controlled by the rate of transport of calcium ions into the leachate solution through the pore structure of the mortar.

With parabolic kinetics, an initial solution may occur at the exposed surface of the mortar (cube). In time, solution proceeds toward the interior of the mortar cube, as the sea water penetrates the pore structure of the cube. In effect, there is a flux of ions in the sea water penetrating the cube toward the center while dissolved species must diffuse out of the cube entering the solution.

The parabolic shape of the calcium release rate curve implies that solution will continue for a long period of time. *KEY POINT* - Since this continuing calcium release is implied, the mixes with lower calcium release would be best from the standpoint of potential for cryptoflorescence damage.

The units on the vertical axis in Figure 35 are micrograms (μg) of atomic species released into solution per gram (g) of mortar specimen in the as-cured condition. The values on the graph are the *differences* between the sea water solution (leachate) concentration after exposure of specific mortar cubes and the starting concentration of species in the sea water solutions[40].

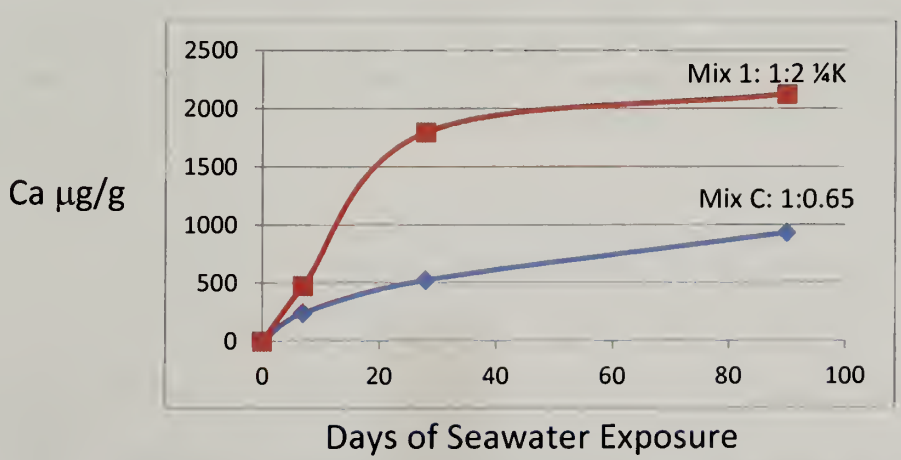


Figure 35: Release of Calcium from Cement-Sand Mortars
(The volumetric proportions in terms of cement to sand are provided)

[40] For clarification, the species in the starting sea water solution were converted to micrograms per gram of the sample (Quantity A) for each test specimen. The concentrations after soaking/leaching for a defined period of time were measured and expressed in terms of micrograms per gram of that specific sample (Quantity B). The result for any specific sample at a given time of soaking was computed as Quantity A minus Quantity B, with a positive number indicating solution of a species into the leachate and a negative number indicating an absorption or "up take" of an atomic species by the specimen.

Alkali metals (sodium or Na and potassium or K) also exhibit solution in sea water (Figure 34). Once again, the solution follows a parabolic relationship, with the potassium solution greater in extent than that of sodium. The Rosendale cement contains a greater concentration of K_2O than Na_2O, so the relative solution behavior is expected.

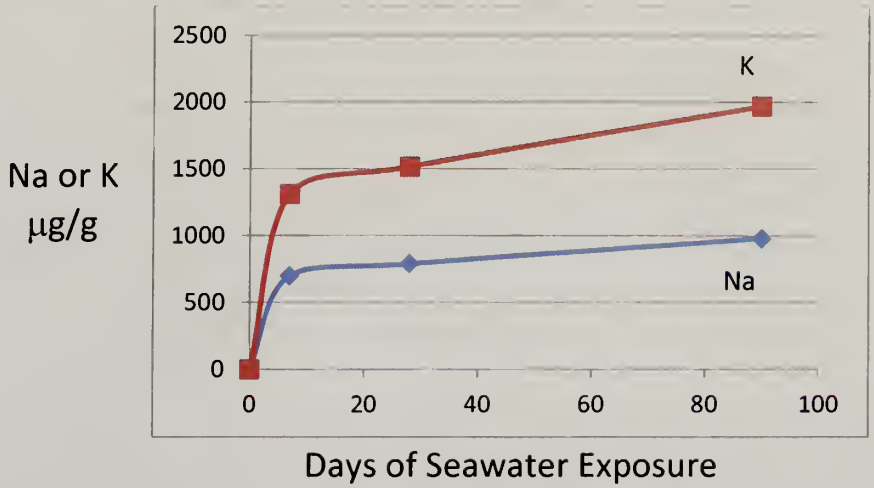


Figure 36: Release of Sodium and Potassium from Mix C (50% Rosendale)

The alkali release from Mix 1 is greater than that of Mix C. The 90-day soaking data is shown in Figure 37 comparing Mixes C and 1. It is interesting that Mix C has the highest alkali solution but the lowest calcium solution of the two cements. In other words, the cement content is apparently controlling the calcium and alkali releases, but they foliow opposite dependencies on cement content.

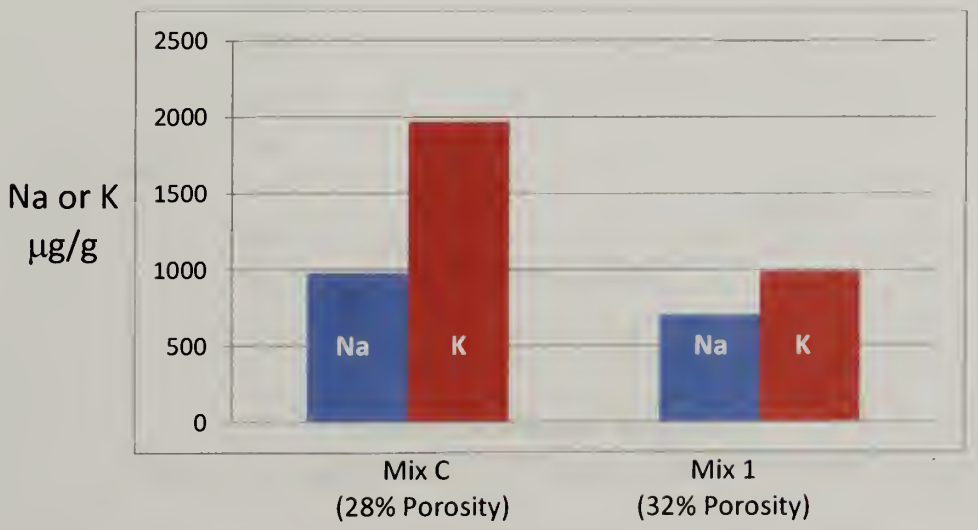


Figure 37: Alkali Solution at 90-days of Submersion for Mixes C and 1

Magnesium exhibits absorption or "uptake" from sea water for Mixes C and 1 (Figure 38). In other words, the concentration of magnesium decreased within the leachate from an initial value during the soaking or leaching process. Both bricks and mortar at FSNM have exhibited magnesium elevation found in forensic analyses.

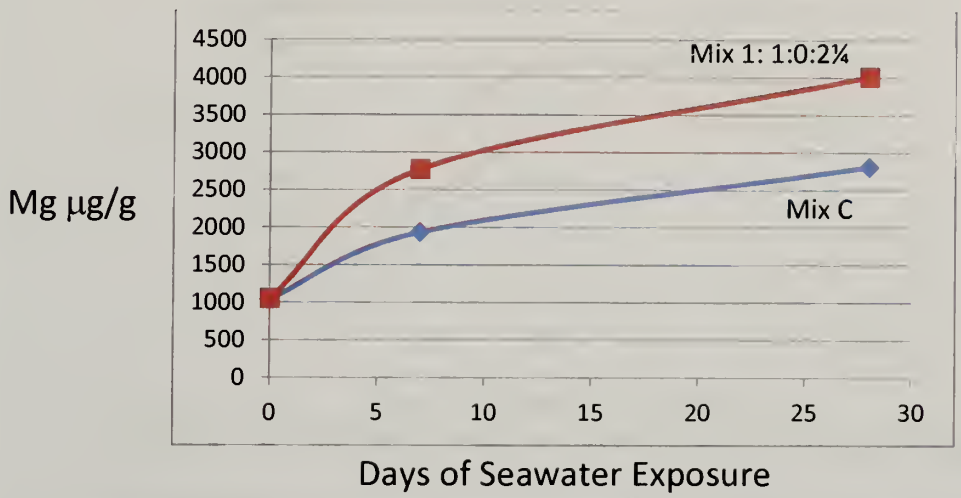


Figure 38: Magnesium Adsorption by Mixes C and 1 through 60 Days

The up take or absorption of sulfate (SO_4) is an example of capture of anionic species by the cement-sand mortars (Figure 39). The magnitude capture and trend is similar for magnesium and sulfate (comparing Figures 38 and 39).

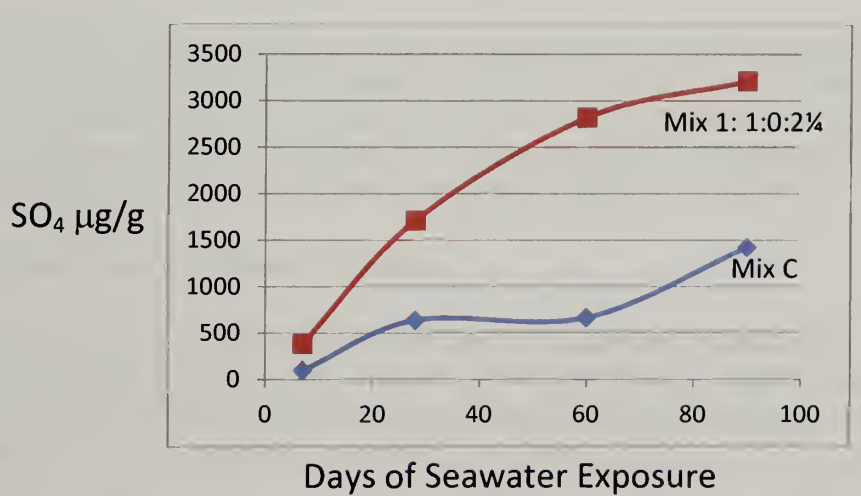


Figure 39: Sulfate Uptake in Cement-Sand Mortar (IC Data)

A different trend is observed for chloride (Cl) absorption as compared to sulfate for Mixes C and 1. In Figure 40, both mixes exhibit initial chloride up take, but Mix 1 exhibits an apparent maximum at about 30 days (there is probably no decrease as the last data point reflects experimental variation). Since the higher cement content mix (Mix C) continues to increase in chloride uptake, the data seems to reflect the influence of cement content in mixes. This

phenomenon may be related to the sand content (lower in Mix C), i.e. the more basic cement (higher pH) has the greater capacity to absorb chloride from sea water.

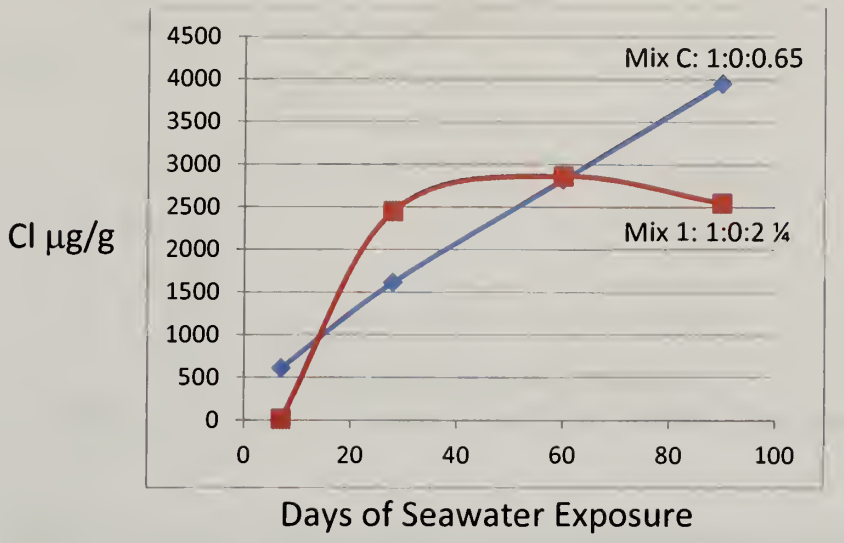


Figure 40: Chloride Uptake in Cement-Sand Mortar (IC Data)

In summary, the cement-sand mortars exhibited calcium solution into the seawater at different rates. The most important factor in calcium release appears to be cement content, with higher cement content releasing less calcium. This result has very important restoration implications, with a strong suggestion that higher cement content is more chemically resistant and has less potential for cryptoflorescence damage in masonry.

The cement-sand mortars exhibited magnesium, chloride and sulfate uptake from the seawater solutions. The cement content apparently affected the ion uptake, with the higher cement mortar absorbing the most chloride but the least magnesium and sulfate. The release and absorption kinetics appear to be parabolic suggesting that the transport of ionic species into or away from mortar cubes is controlled by the rate of diffusion in solution.

High Calcium Lime Containing Mortars

Like the cement-sand mortars, the mortars containing high calcium lime, Mixes 2 and 3, exhibited solution of alkalis and calcium while absorbing magnesium, sulfur and chloride (Figure 41). The solution and absorption kinetics follow parabolic rate relationships. The magnitude of calcium solution increased the lime content in HC containing lime mortars (Table 32).

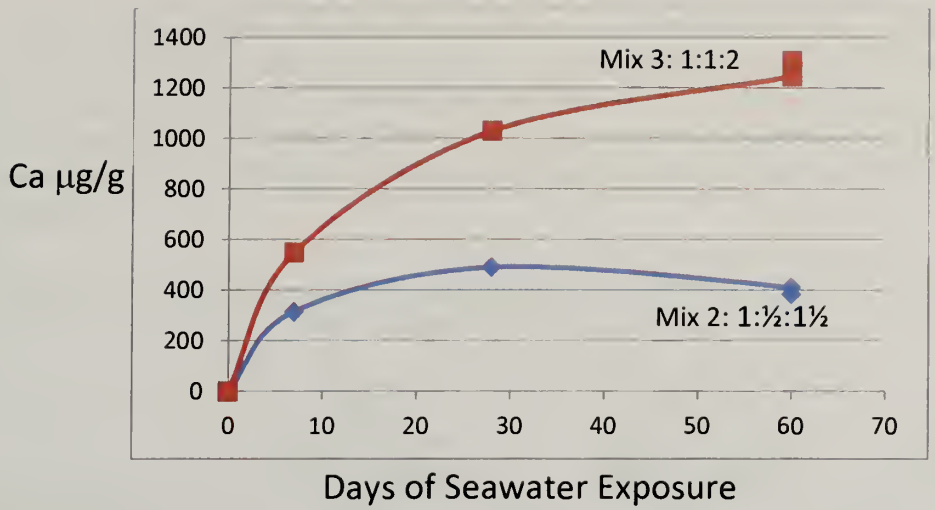


Figure 41: Calcium Solution from High Calcium Lime Mortars

Table 32: Comparison of Calcium Solution (µg/g) from Mixes 2 and 3

Exposure, days	Mix 2 (12.6% lime) 28.6% porosity	Mix 3 (19.0% lime) 34.8% porosity
7	315	549
14	491	1030
28	412	1248
90	286	1308

The mortars containing HC lime exhibited similar magnesium uptake (Figure 42). The same was true for alkali solution (not shown).

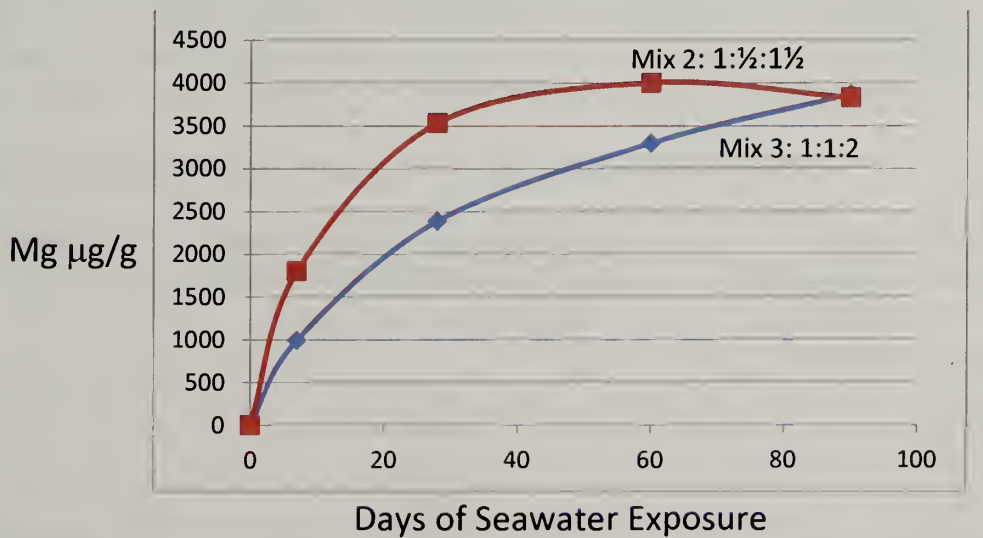


Figure 42: Magnesium Uptake from High Calcium Lime Mortars

The HC lime mortars absorbed both sulfate and chloride from the seawater solutions, but the presence of the lime in the mortars lead to a much greater uptake of the anions than in the cement-sand mortars. In Table 33, the 60-day absorption of sulfate and chloride are compared for Mix 1 (no lime), Mix 2 (12.6% HC lime) with Mix 3 (19% HC lime). The data shows sulfate absorption to increase as HC lime content is increased, but the chloride absorption trend is in the opposite direction.

Table 33: Sulfate and Chloride Absorption as Affected by Mortar Composition At 60 Days of Immersion (IC).

	Mix 1 0% HC lime 32.1% porosity	**Mix 2 12.6% HC lime 28.5% porosity**	**Mix 3 19.0 % HC lime 34.8% porosity**
Sulfate absorption μg/g	2819	3598	4370
Chloride absorption μg/g	2865	1517	1318

Since parabolic kinetics are involved, the rates of solution or absorption are controlled by the transport of species through the pores of the mortar in aqueous solution. Since the ionic species are charged, it follows that there must be a zero net accumulation and loss of charged species either within the mortar or within the leachate solution. It is possible to use the major cationic species to determine if charge neutrality is observed, whereas, it is impossible to do this with anions because negative carbonate ions (CO_3^{2-}) in solution were not quantified.

For Mix 2, the net accumulation of charge within the mortar is determined by calculating the equivalent weights (mass/charge as microequivalents of μeq)) for each species at a dwell of 60 days of immersion (Table 34). This from a standpoint of mass change for major species involved in mass transfer, there is a net increase in mass of cationic species but there is effectively no change in charge, i.e. there is no accumulation of charge as would be expected.

Table 34: Comparison of Mass and Charge Migration in Mortar 2 at 60 Days of Immersion

Species	**Mass Migration by Quantity absorbed (+) or Dissolved (-) per gram of mortar in μg/g**	**Charge Migration by Milliequivalent weight absorbed (+) or dissolved (-) per gram of mortar in μeq/gram**
Ca^{2+}	-412	-5.14
Mg^{2+}	+3301	+68.08
K^{-}	-2112	-54.0
Na^{+}	-208	-9.05
Net Change	569	$0.11 \approx 0$

In summary, the HC lime mortars exhibited parabolic solution kinetics with the loss of calcium tracking the lime content of the mix. The data indicates that the solution and absorption phenomena results in no net charge accumulation in the mortar or leachate solution. Cations contribute to the mass of the mortars through magnesium solution (overriding loss of calcium, sodium, and potassium). It is likely that sulfate and chloride absorption are overridden by carbonate loss (via carbonate dissolution), but this was not confirmed as carbonate ions in solution were not monitored.

1. Dolomitic Lime (DL) Mortars

Dolomitic lime mortars exhibited greater release of calcium than mortars of similar proportions made using lime putty. The calcium release of all DL mortars was similar, i.e. content of dolomitic lime did not influence calcium release. Magnesium absorption was similar in the DL mortars (Figure 43).

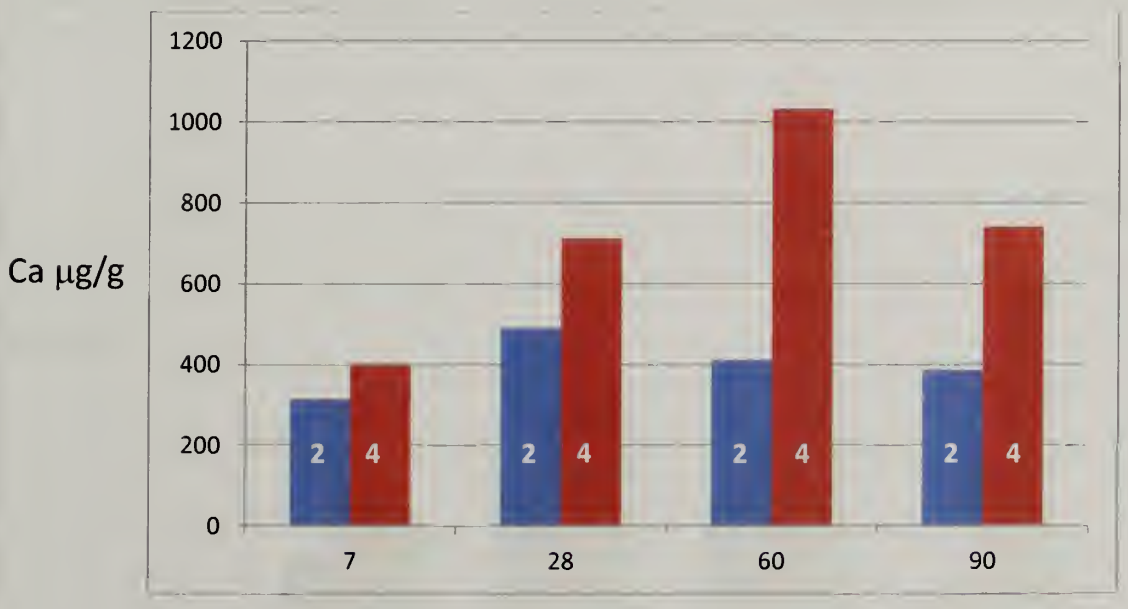
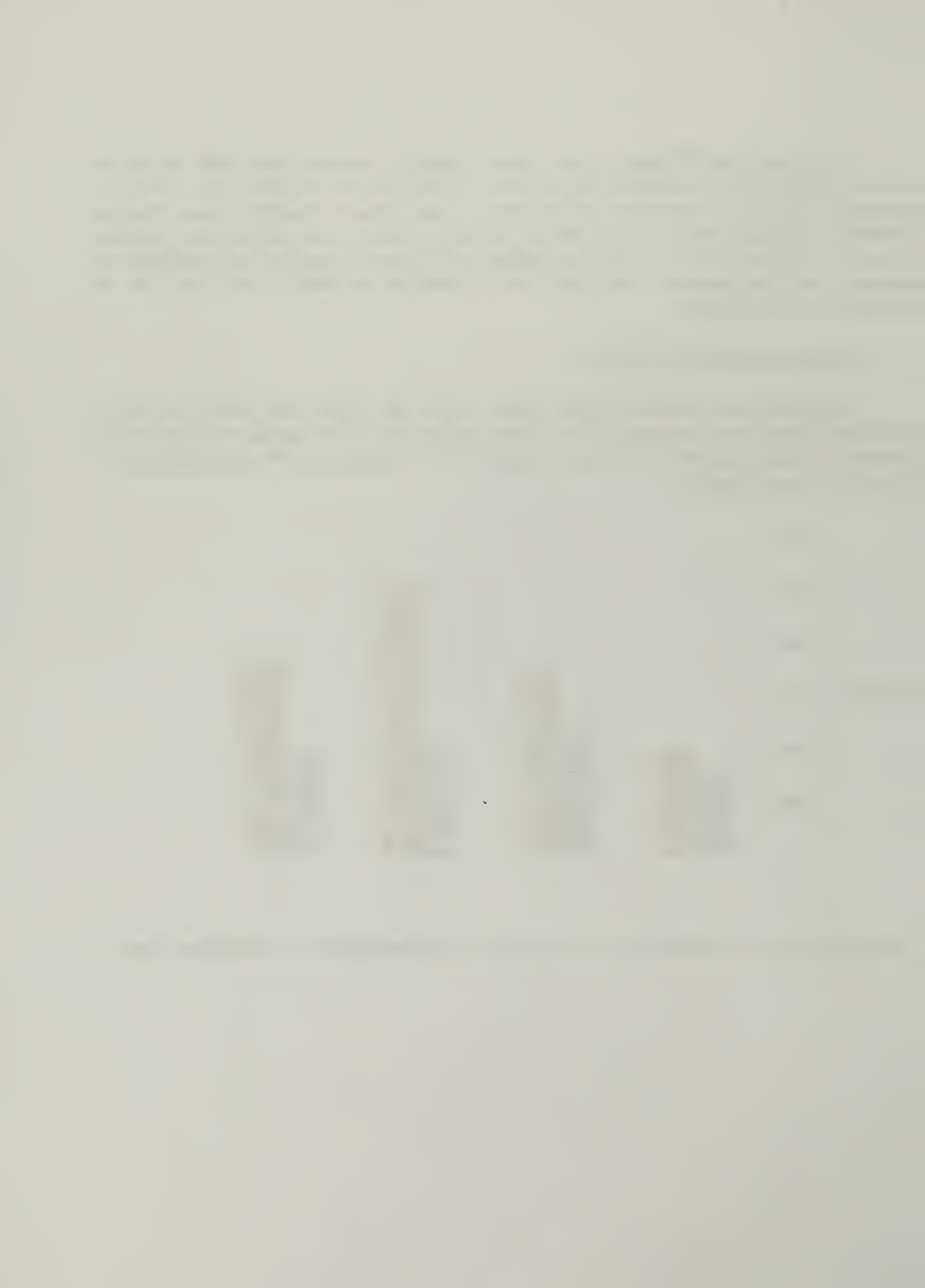


Figure 43: Calcium Solution for HC Lime (Mix 2) and Dolomitic Lime (Mix 4) at 7 Days



2. Effect of Density and Porosity

The series of Mixes 2, 6, and 7 were mortars of the same volumetric proportions (1:½:1½) but made with different water contents so as to simulate normal bedding mortar (Mix 2), manual pointing mortar (Mix 6), and a mortar for grout bag application (Mix 7). The properties of mortar cubes made from these mixes are given in Table 35.

Table 35: Cured Mortar Properties as a Function of Water Content (1:½:1½ Mixes)

Mix	Density, Cured g/cm3	Apparent Porosity, %	Fraction of Pores <1μ
6	1.97	24.5	92.1
2	1.86	28.6	964.9
7	1.73	30.4	88.9

The differences in density and porosity did not significantly affect solution of any species monitored except for calcium (Figure 44), a case where IC and ICP data were in agreement. This result additionally suggests that the interaction of the mortar cubes and sea water involves subsurface phenomena when calcium solution was involved.

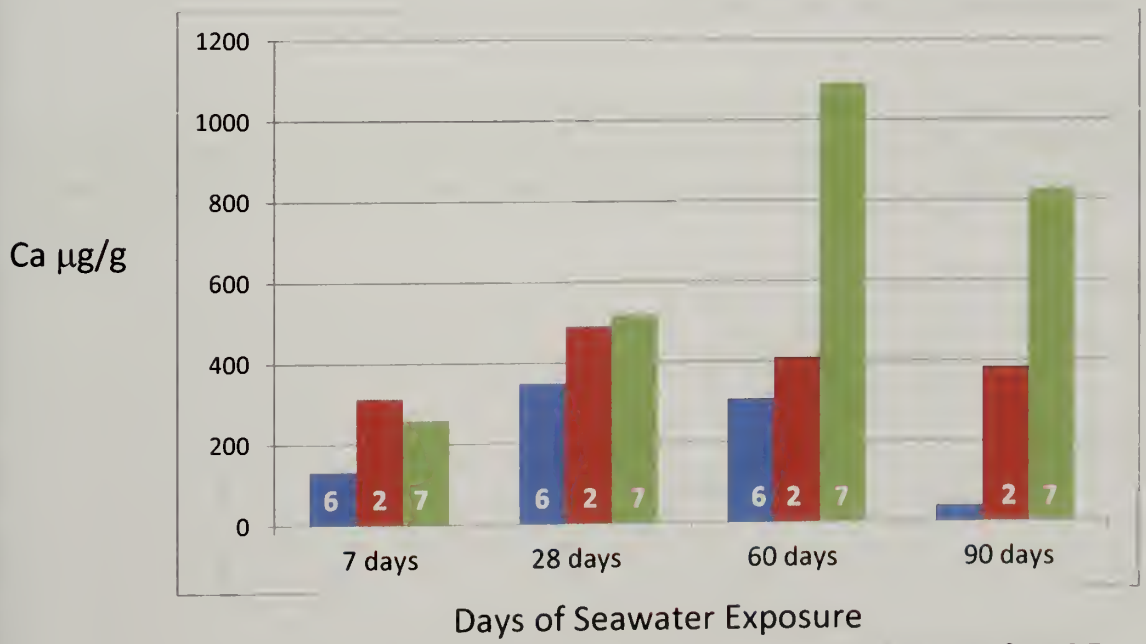


Figure 44: Comparison of Calcium Leaching for Mixes 6, 2 and 7

3. Total Weight Change Due to Sea Water Immersion

The total weight losses of the mortar specimens are given in Table 36 at 90-days of immersion in sea water. All mortars lost weight as might be expected from the decomposition of carbonate phases in the presence of sea water. In effect, this could be called "total corrosion loss."

Table 36: Weight Loss of Mortar Specimens at 90 Days

Mix	Mix Goal Cement:Lime:Sand Volume	Cement Goal %	AP %	Weight Loss, %
C	1:0:0.65	50.0	28.46	5.79
1	1:0:2¼	21.1	32.14	2.51
2	1:½:1½	26.4	28.65	4.21
3	1:1:2	19.85	34.81	2.88
4	1:½:1½	28.25	28.20	4.14
5	1:1:2	22.07	29.83	3.93
6	1:½:1½	26.4	24.56	3.07
7	1:½:1½	26.4	30.42	3.40

The highest weight loss was the mix with the highest cement content. When weight loss is plotted versus cement content of the mixes, there is a suggestion of a correlation (Figure 45). There is little correlation between sand content and porosity with weight loss on sea water immersion.

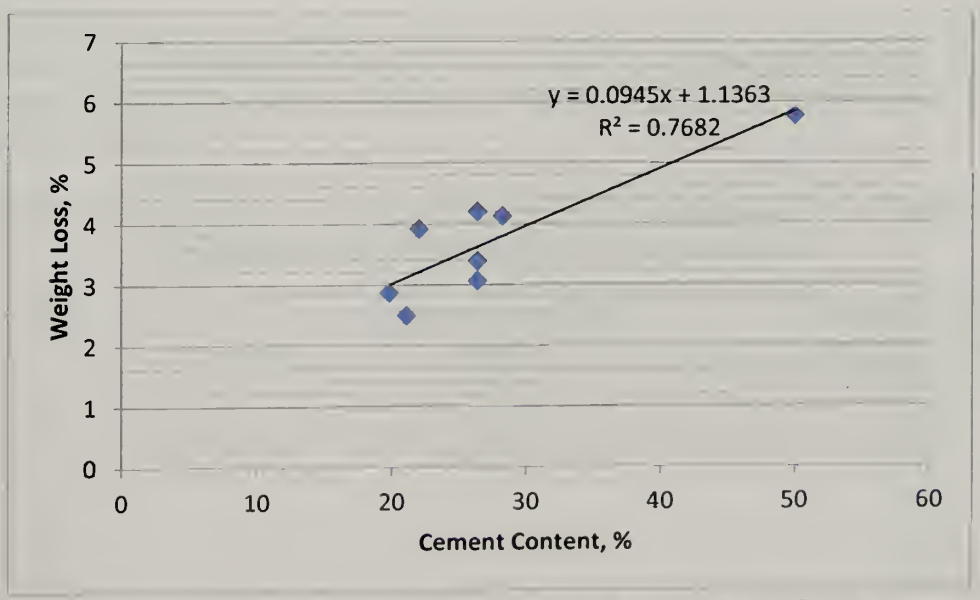


Figure 45: Correlation of Weight Loss and Cement Content

4. Dimension Changes on Sea Water Soak

Linear changes were measured on individual mortar cubes after soaking for periods of seven to 60 days, and these expansions were expressed as a percentage change in dimension (change in length/original length X 100) for the width, length, and height dimensions of cubes. Length measurements were with calipers. The data for the length dimension for mixes C and 1 (no lime) are shown in Figure 46.

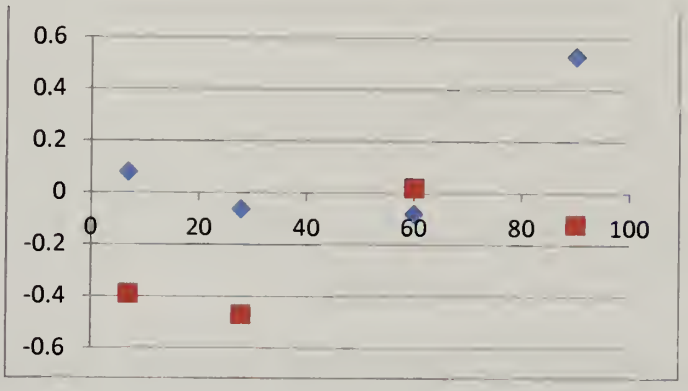


Figure 46: Expansion Data (as %) for Mixes C (Blue or ◆) and 1 (Red or ■)

The data implies an initial shrinkage followed by expansions as the interaction with sea water progresses from the surface of cubes toward the interior of the specimens by penetration in the pore structure of the mortar. The data suggests that higher expansions may be possible at the highest natural cement level (Mix C). In general, however, there was considerable scatter in the data suggesting a better technique of measuring specimens after soak is required.

It is interesting that mixes with higher sand content exhibit either lower expansion or greater shrinkage when comparing Mixes C and 1, 2 and 3, or 4 and 5 (Table 36). This suggests that sand forms a physical network of aggregate within the mortar constraining the mortar from expansion or shrinkage.

Table 37: Average Linear Change after Sea Water Immersion for All Immersions
(Expansion is positive and Shrinkage is negative)

Mix	Cement:Lime:Sand Volume	Linear Change, % Length Dimension
C	1:0:0.65	+0.49
1	1:0:2¼	-0.96
2	1:½:1½	0.34
3	1:1:2	0.02
4	1:½:1½	-0.10
5	1:1:2	-0.20

There may be a correlation between weight loss and linear change on sea water immersion (Figure 47). The correlation coefficient ($R^2 = 0.62$) indicates a weak correlation, and this result may also reflect errors in measurements.

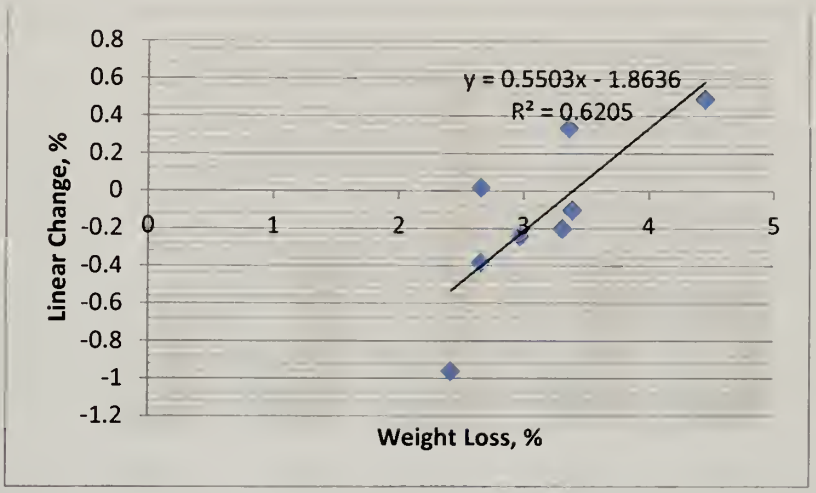


Figure 47: Linear Change on Sea Water Immersion Plotted Versus Weight Loss

5. Leaching in Dilute Hydrochloric Acid

In all cases, the pH of leachate solutions increased from an initial value of 1.34 (zero immersion time) to the range of 7-8 in 7 days (Figure 48). All of the mixes tested exhibited similar behavior. Additions of lime to mortar mixes did not affect the pH change over time. The results simply show a process of neutralization by the mortar on the leachate solution – a process frequently observed when performing TCLP tests on concrete specimens.

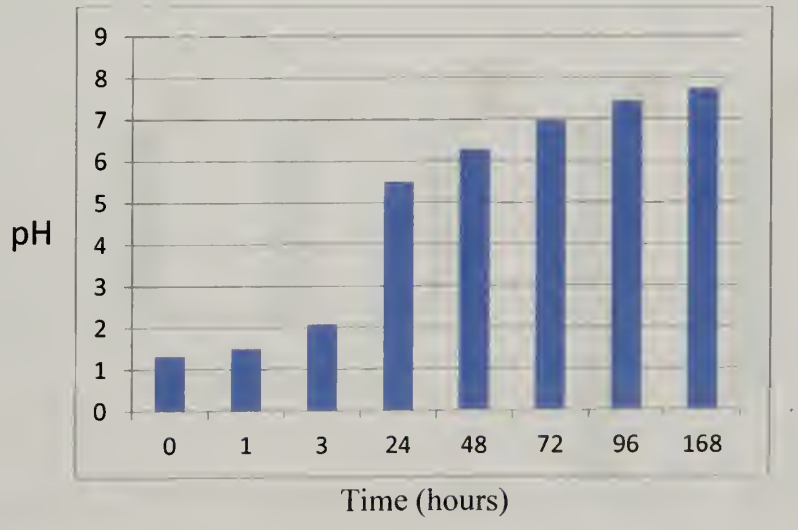


Figure 48: Change in pH With Immersion Time for Mix C in 7 Days

The acid immersions dissolved significantly more calcium in seven days as compared to sea water (Figure 49). This implies that acid cleaning of masonry after pointing with natural

cement mortars has a very high potential for efflorescence discoloration and a potential for cryptoflorescence damage to bricks.

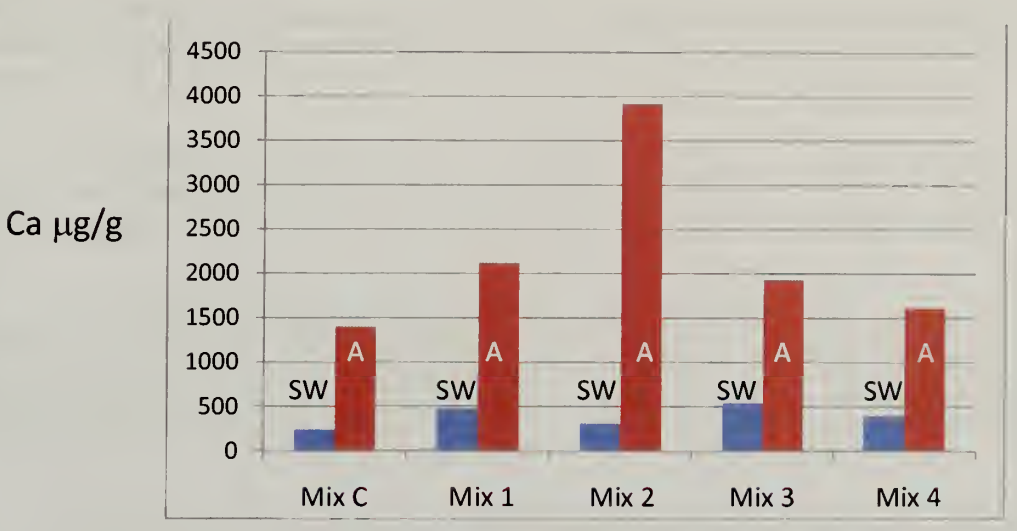


Figure 49: Comparison of Calcium Leaching Between Sea Water (SW) and Dilute HCl (A) at 7 Days

Interestingly, acid immersion resulted in magnesium loss or leaching from mortar mixes that all exhibited magnesium uptake in sea water immersion (Figure 50). The same "flip-flop" in behavior was found with sulfur uptake in sea water and sulfur loss in dilute acid immersions. In contrast, sodium and potassium exhibited leaching in both sea water and acid.

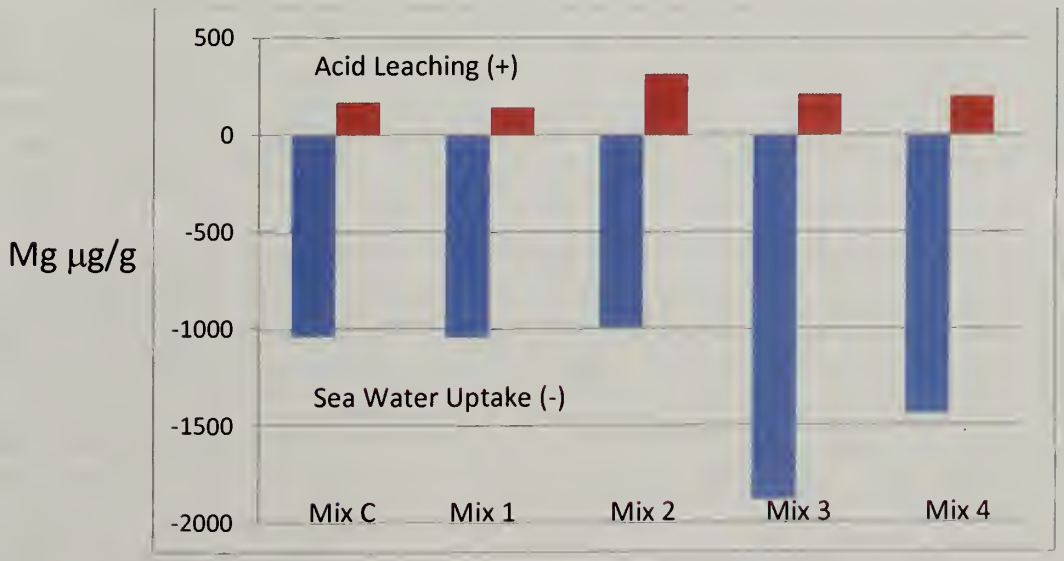


Figure 50: Opposite Behavior for Magnesium in Sea Water and Acid

Summary of Mortar Interactions with Seawater

All mortar specimens exhibited solution of sodium, potassium, and calcium amount released a function of soaking time in seawater. For cement-lime mortar, the amount of calcium released increased with lime content. Calcium release was influenced by density and porosity, with less release over time from higher density/lower porosity mixes.

All mortars absorbed sulfate and chloride from the sea water solutions with chloride uptake continuing over long exposure periods, and this was particularly notable for mixes high in cement content. By contrast, sulfate uptake tended to reach a maximum over time.

All mortars exhibited magnesium uptake, a fact possibly reflecting the affinity of magnesium in solution for surface absorption on sand and/or Rosendale cement. The magnesium uptake dominated exchange of cationic species with seawater resulting in a net increase in the weight of cationic species within the mortars. However, it is likely that carbonate solution led to a net decrease in weight of specimens over time resulting in corrosion loss.

Since the kinetics of solution and absorption exhibited parabolic relationships with time, the rates of solution and absorption are controlled by transport of ions into or from the mortar. In the initial stages of exposure, solution is primarily from the exposed surface of the mortar. Over increasing immersion time, solution takes place behind the exposed surface and within the mortar's porosity resulting in the parabolic kinetics. The mobility of ions may be limited by ionic charge considerations, as net charge changes locally due to ion migration are not allowed, i.e. movement of charged species into the mortar must be counterbalanced by movement of an equivalent quantity of charged out of the mortar.

There is a reasonable suggestion that the highest weight loss on sea water immersion is observed in the mixes with higher Rosendale cement contents. This fact further suggests that for restoration, greater solution durability is achieved with mortars containing lime, but lime containing mixes also exhibit greater calcium solution potentially influencing cryptoflorescence. There is a strong suggestion that the sand content of the mortar influences the tendency of the mortar to expand or shrink on immersion in sea water.

The important implication for restoration of historic structures is that the higher cement level mortar without lime exhibited the least solution release of calcium in sea water. Since calcium solution has been linked to cryptofluorescence damage to bricks by a "scaling process", minimizing the solution release of calcium is particularly important in the repair and restoration of historic brick masonry buildings. Specifically, for seawater contact and in cases of rising damp (including ground salts), Rosendale cement should be strongly considered at higher cement levels (near 50% by weight) for masonry pointing or for replacement bedding mortars. This result agrees with Italian experience of using mortars with pozzolanic components below areas of rising damp in Venice[41,42].

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[41] L. Greco, C. Mazzetti, and P. Periani, New findings and precautions concerning decomposition of cement mortars and conglomerates, Giornale del Genio Civile 89 (1951) 3-14.

The results of this study show that dilute acid, as might be used in masonry cleaning after pointing repairs, renders both calcium and magnesium as soluble. Experience shows that such solution leads to efflorescence discoloration of masonry, and it may lead to cryptoflorescence damage in bricks. Therefore, care is advised when considering cleaning of masonry, and thorough prewetting of the masonry wall with potable water is appropriate when acid cleaning of masonry (or use of commercial cleaners) is necessary. In these cases, it is advisable to clean a small test area to observe results after a drying period prior to use of cleaning solutions on larger and visible areas.

In this Chapter, it is clear that restoration involves trade-offs considering technical properties. Higher cement content provides lower calcium solution (potentially of benefit to the masonry) but potentially lower durability thus requiring more frequent maintenance of the masonry by pointing. Higher sand content may reduce expansion on sea water contact so as to benefit durability. Additions of lime to natural cement mortars – of clear benefit in improving workability of mortar – increases calcium solution.

The overall conclusion is that high cement content mixes of Rosendale cement and sand are the best choice for masonry restoration in the presence of constant contact with salts in water solution from sea water contact or rising damp.

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[42] F. Venaile, M. Setti, C. Rodriques-Navarro, S. Lodola, W. Palestra, and A. Busetto, Thaumasite as decay product of cement mortar in brick masonry of a church near Venice, Cem. Concr. Compos. 8 (2003) 1123-1129.

Freezing and Thawing Durability Assessment of Mortars

Freezing and Thawing Test Results

Preliminary experiments were conducted with excess mortar cubes of Mixes 3, 4, and 5 to observe the test method so that observation intervals could be anticipated. In other words, Method C666 calls for specimens to be examined on a frequency not to exceed 36 cycles of freezing and thawing, but more frequent observation is required if failures occur in less than 36 cycles. A typical record of temperatures during the experiments is given in Figure 51.

In these preliminary experiments, the specimens tested all exhibited damage after only three cycles. In the case of mixes 3 and 5, the specimens were soft to a fingernail indention and they exhibited crumbling in areas below the water line in the pans of the apparatus. Mix 4 exhibited delamination on a plane in the specimen at the water line elevation in the pans, i.e. the top portion of the specimen separated from the immersed end or bottom. Because of this preliminary observation at three cycles for a few specimens, the formal testing program of all specimens was begun and interrupted at six cycles for a first observation.

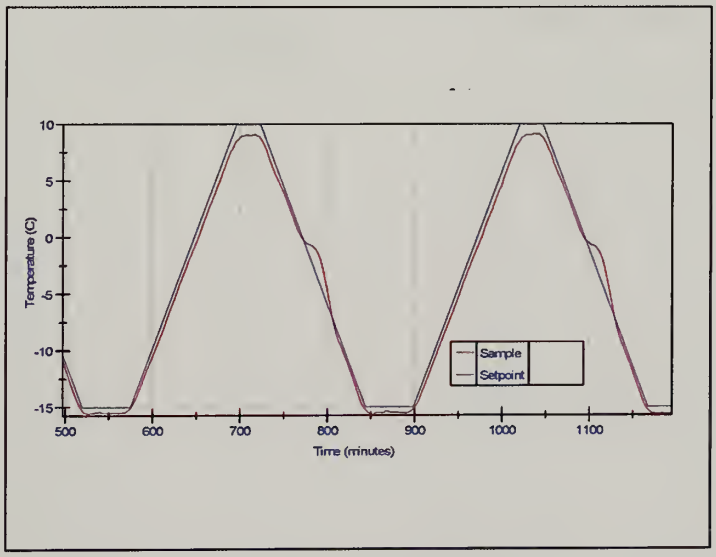

Figure 51: Thermal Measurements during C666 Freezing and Thawing Cycles

The results of six cycles of freezing and thawing are summarized in Table 38. At six cycles, the major failures observed were due to cracking – particularly near the elevation of the water line for specimens. This suggests that a differential expansion phenomenon on freezing of water within the specimens was a contribution to early failure. In addition, specimens that failed generally exhibited a surface condition soft to the scratch of a fingernail. It is interesting that the specimens (Mixes 3, 4, and 5) that failed in three cycles in the preliminary testing also exhibited failure in the testing program (when repeated) at 6 cycles. See Figures 52-55.

Table 38: Freezing and Thawing Assessment in Method C666 at 6 Cycles

Mix	Composition	Assessment at 6 Cycles	Figure	Comment
C	1:0:0.65 (bedding)	Unaffected. Testing continued.	55	Unaffected.
1	1:0:2¼ (bedding)	Failed. Testing stopped.	55	Crack through in specimen 2.
2	1:½:1½ (bedding)	Failed. Testing stopped.	56	Delamination at water line, specimen 3.
3	1:1:2 (bedding)	Failed. Testing stopped.	57	Delamination below/at water line specimens 2 and 3.
4	1:½:1½ (bedding, dolomitic lime)	Failed. Testing stopped.	58	Delamination specimens 2 and 3. Severe damage specimen 3.
5	1:1:2 (bedding, dolomitic lime)	Failed. Testing stopped.	58	Cracking, delamination specimen 3.
6	1:½:1½ (manual pointing)	Unaffected. Testing continued.	56	Unaffected.
7	1:½:1½ (grout bag pointing)	Slight damage. Testing continued.	56	Slight damage.

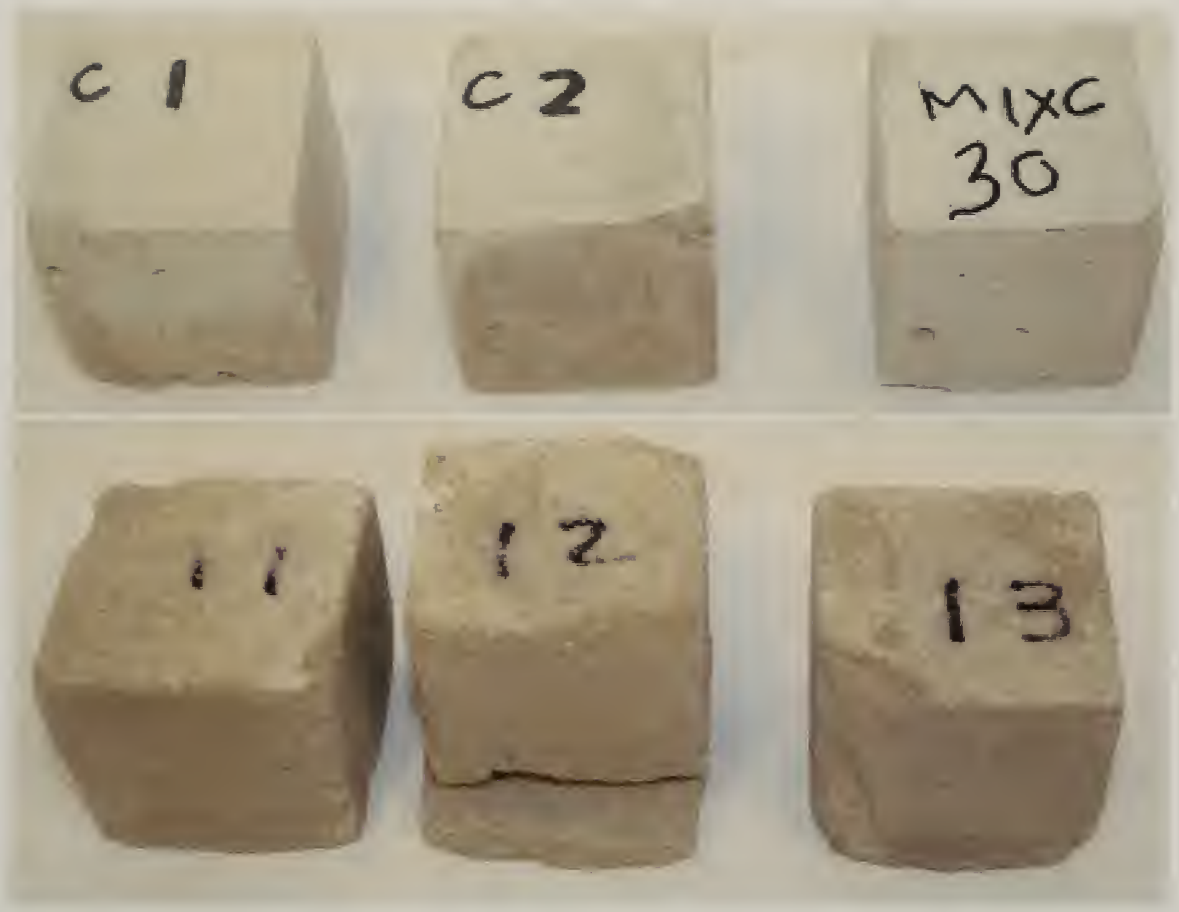

Figure 52: C666 Results for Mixes and 1 at 6 Cycles (Mixes Contain No Lime)
Note: Mix 1 Judged as Failed; Mixes C judged as unaffected and continued in testing.

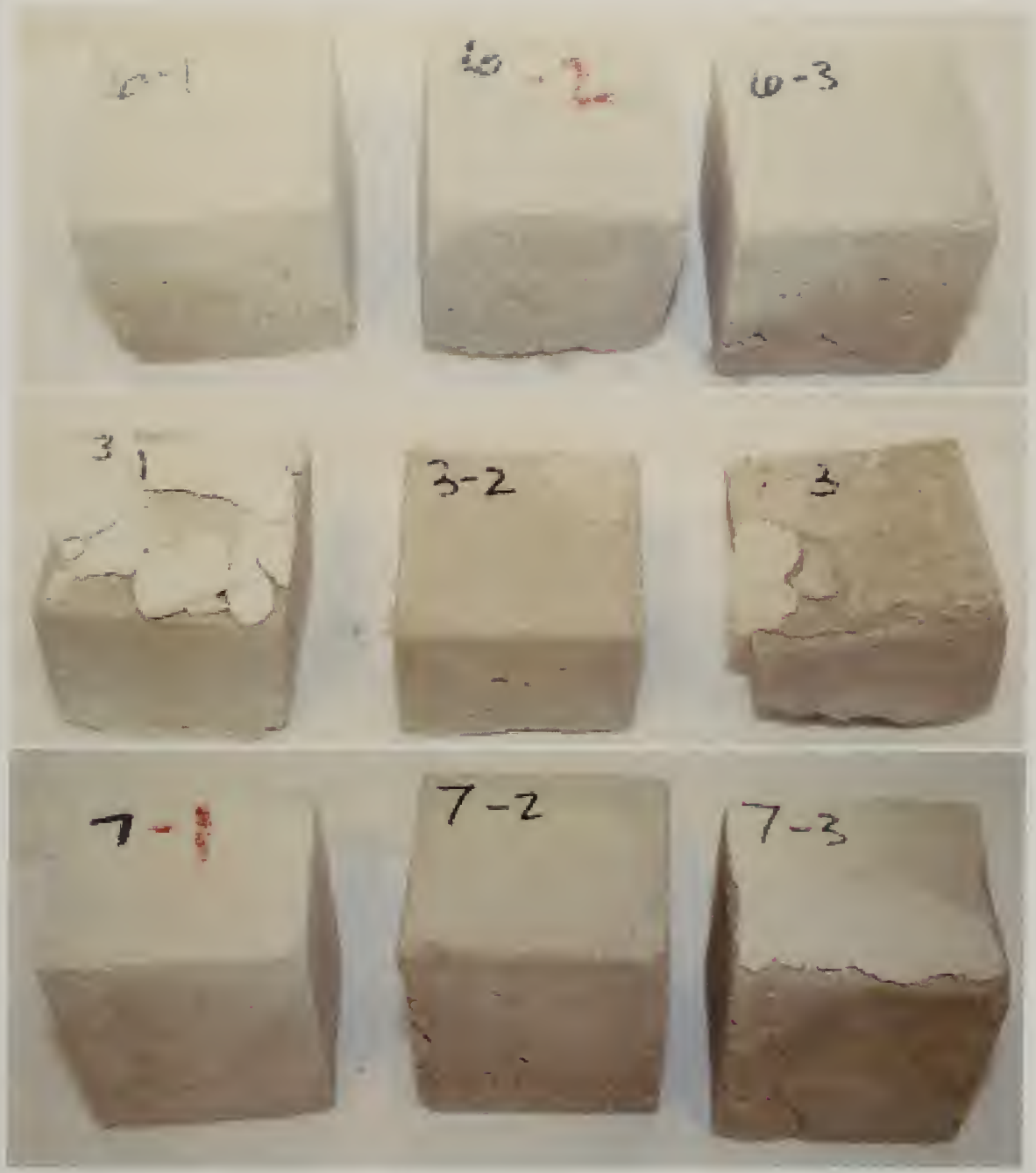

Figure 53: C666 Results for Mixes and 1 at 6 Cycles (All 1:½:1½ at different water contents). Note: Mix 3 Judged as Failed; Mixes 6 and 7 Judged as damaged but continued in testing.

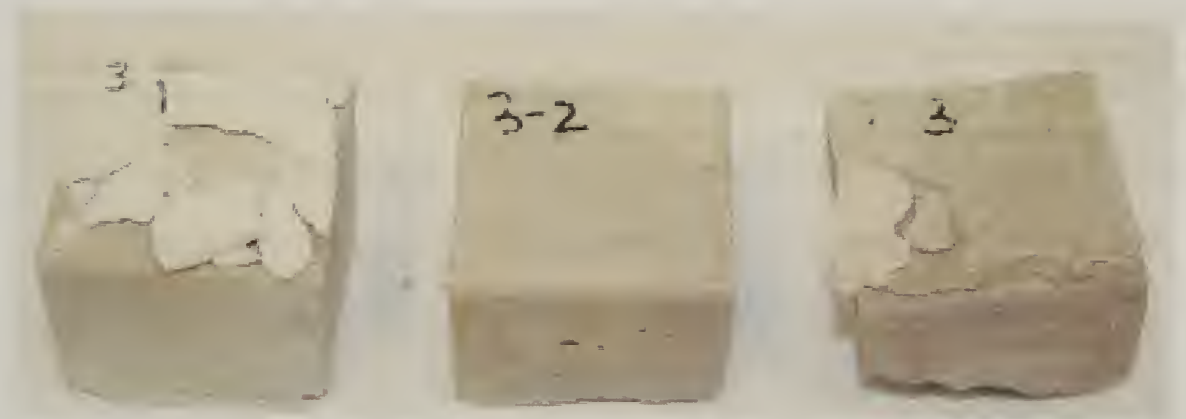

Figure 54: C666 Results for Mixes 6 at 6 Cycles (1:1:2) – Judged as Failed

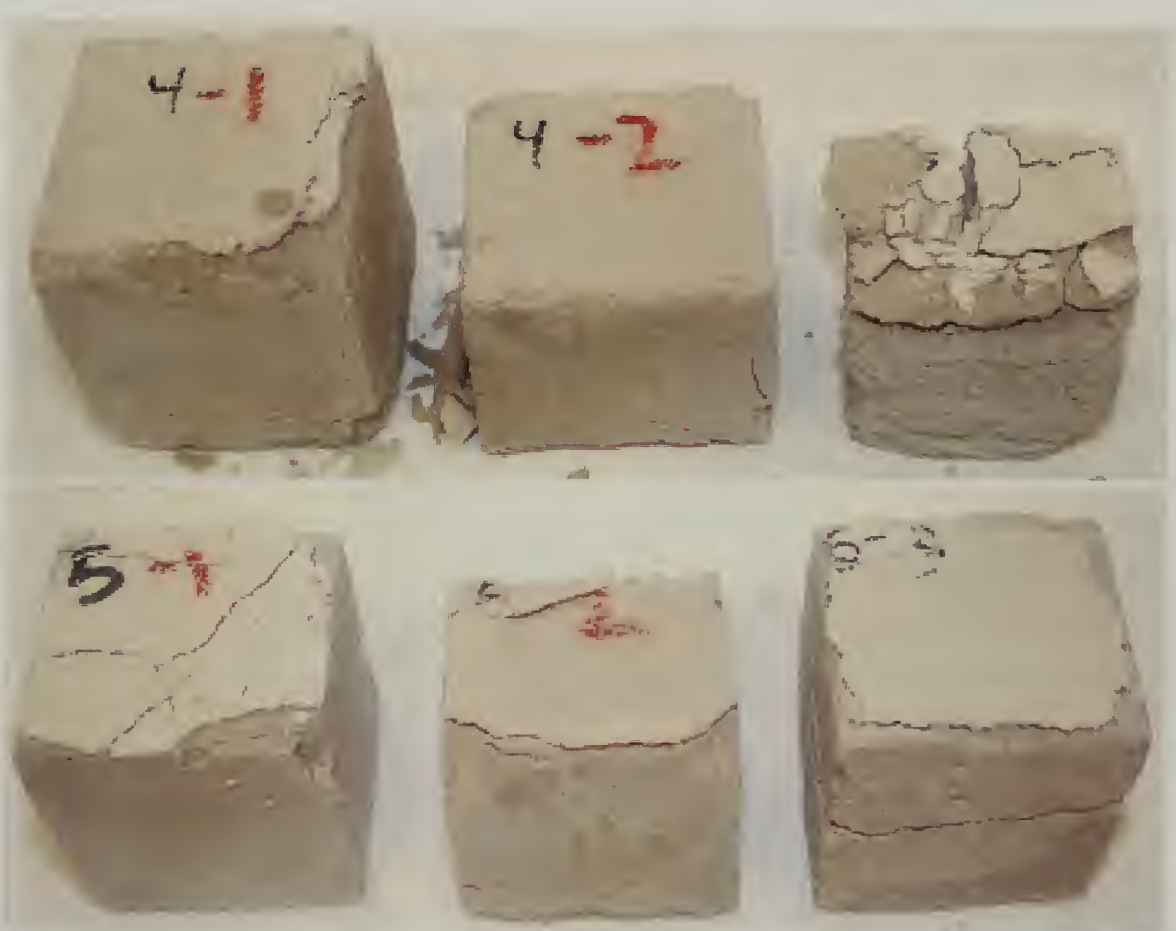

Figure 55: C666 Results for Mixes 4 and 5 (contain dolomitic lime) – Judged as Failed at Six Cycles

Specimens C, 6, and 7 were subjected to additional C666 freezing and thawing cycles to obtain a total of 24 cycles. The results are summarized in Table 39, with the condition of mortar cubes shown in Figures 56-57. It was apparent that the specimens, in continued testing to 24 cycles, primarily exhibited cracking and delamination suggesting that the mechanism of failure changed or was exaggerated so that failure was primarily below the water/ice line or elevation.

Table 39: Freezing and Thawing Assessment in Method C666 at 24 Cycles

Mix	Composition	Assessment at 24 Cycles	Figure	Comment
C	1:0:0.65 (bedding)	Specimen affected. Testing continued.	59	Rounding of the bottom corners of the specimen (below the water line) and cracking was observed
6	1:½:1½ (manual pointing)	Failed. Testing discontinued.	60	Extreme corner rounding below the water line and cracking was observed for all specimens
7	1:½:1½ (grout bag pointing)	Failed. Testing discontinued.	60	Extreme corner rounding below the water line and cracking was observed for the majority of specimens

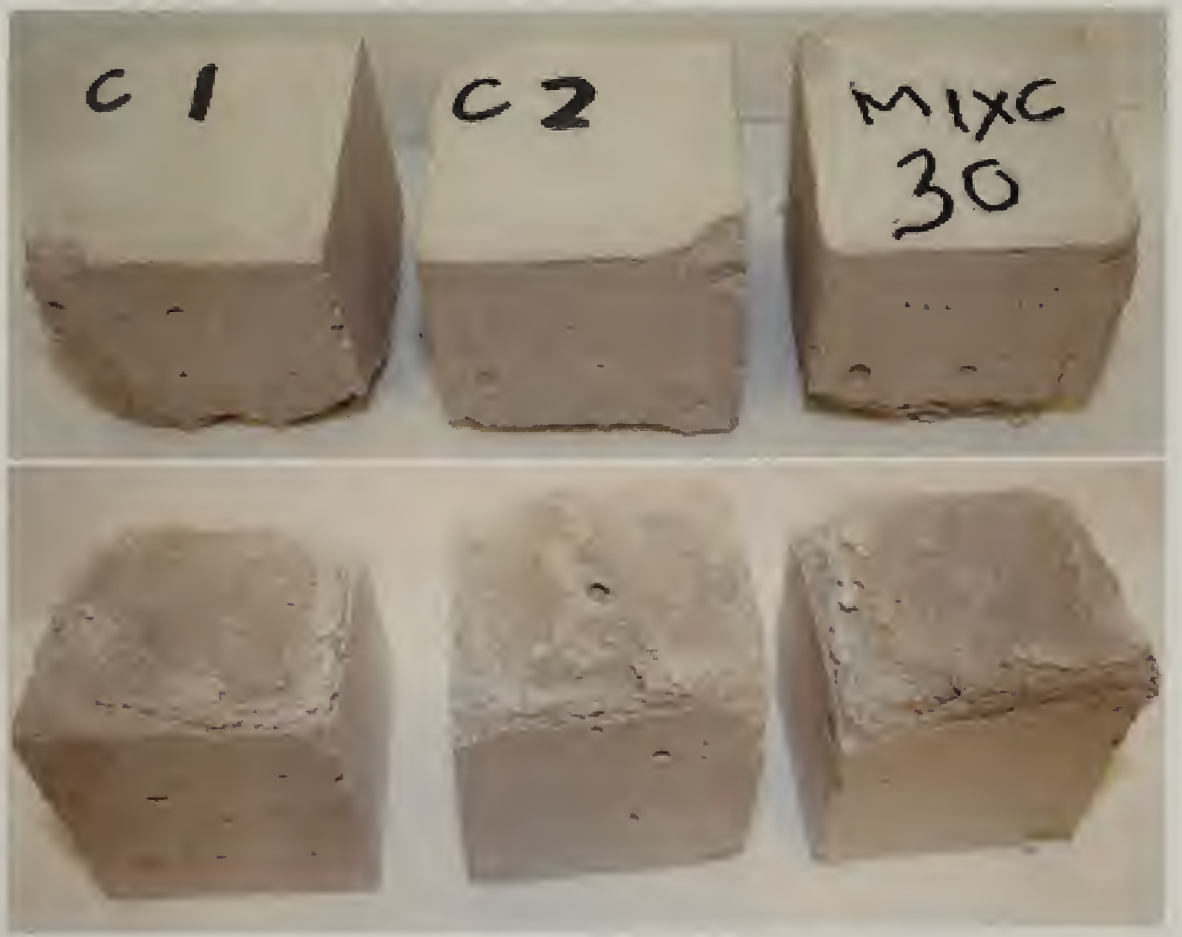

Figure 56: C666 Results for Mix C at 24 Cycles

Figure 57: C666 Results for Mixes 6 and 7 at 24 Cycles (Inverted Cubes)

Freezing and thawing tests continued for Mix C until a total of 50 cycles w
and the test specimens after this regime are shown in Figure 58. At this point Mix
rounding of the bottom corners and edges with delamination in progress, so the spec
deemed as "failed" and testing was terminated.

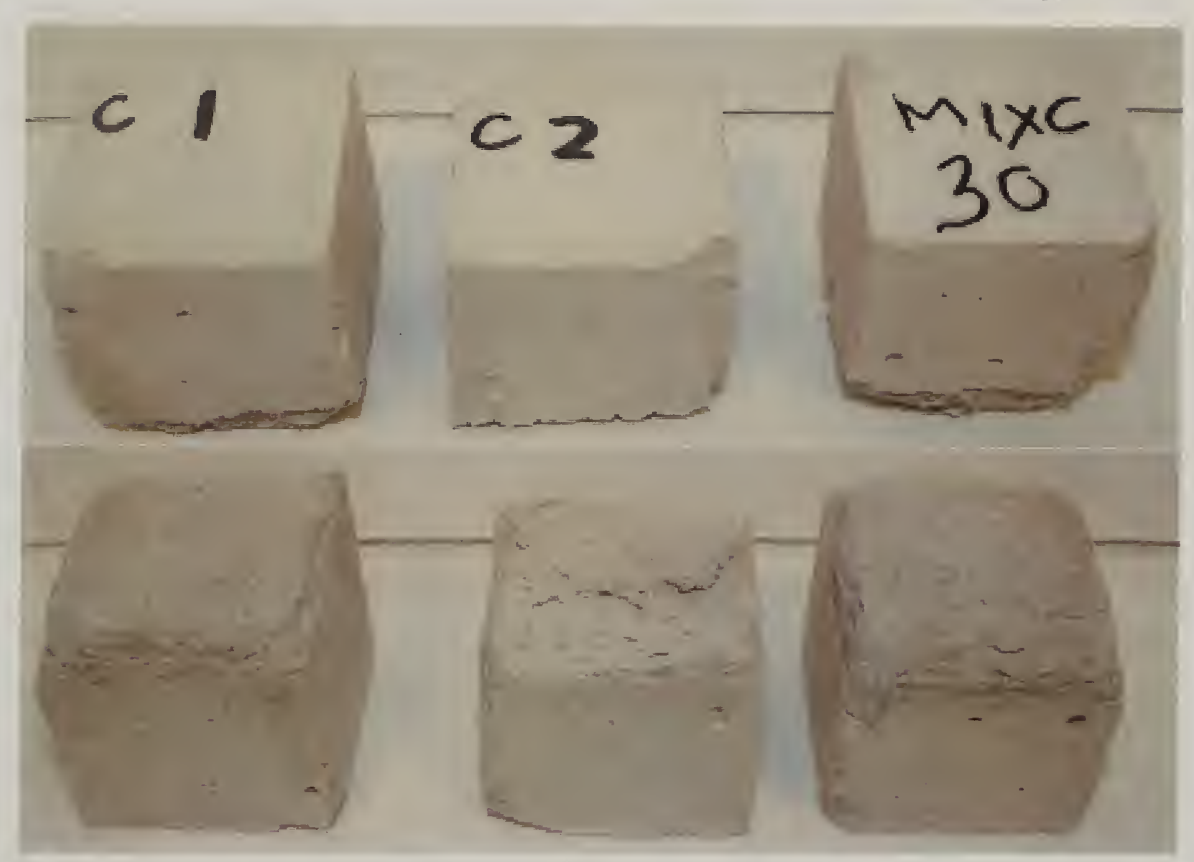

Figure 58: Mix C at 50 Cycles

Discussion of Results

The results of testing clearly show:

- Some mortar mixes exhibited extremely low resistance to freezing and thawing with failure before or when six cycles were obtained. These mixes exhibited cracking and delamination with poor scratch resistance.
- Most of the mortar mixes exhibited an intermediate resistance to cycling. These specimens exhibited cracking and delamination, and many specimens exhibited rounding of corners (within the immersed portion of the specimens).
- The highest cement content mix (without lime) achieved 50 cycles. At this point, the specimen corners exhibited rounding (within the immersed portion of the specimens).

The behavior of the specimens that survived six cycles and continued for additional cycles suggests that the expansion of water within the immersed portions of specimens contributed to the failure mechanism. It is well known that the volumetric expansion of water on freezing is about 11%. Water within the pores of a material will cause the material to expand on freezing[43] (in three dimensions). Thus, the immersed portion of the specimen undergoes a volume expansion on freezing relative to the portion of the specimen above the elevation of the water/ice line (as the top of the specimen is of lower saturation). The situation is illustrated in Figure 59, where the red arrows represent expansions within the material in this two dimensional representation.

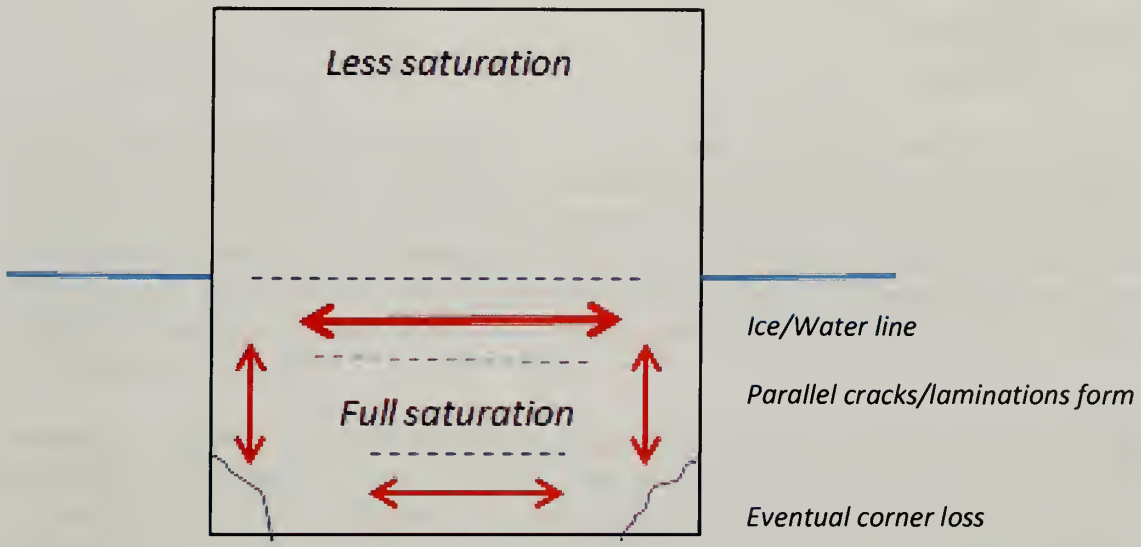

Figure 59: Stresses due to Expansions within a Mortar Cube during Freezing

The differential stress situation tends to cause cracking more or less parallel to the water/ice line (blue line), and the laminations/cracks occur parallel to one another. The second consequence of repeated cycles is loss of specimen corners and edges, illustrated in Figure 61 by jagged lines at the specimen corners. The latter effect is due to the stresses as the bottom of the specimen expands attempting to form a truncated pyramid shape. The final result is a loss of bottom edges and bottom corners on the specimens.

The progression of failures in cyclic testing appears to depend on the strength of the specimens (Table 40). Specifically, the tensile strength seems to tract performance better than compressive strength. Since all specimens exhibited similar apparent porosities and similar fractions of porosity <1 micron in diameter, the strength of the mortar mix appears to be the strongest influence in freezing and thawing performance.

[43] Eric Seaverson, "Predicting Freeze Thaw Durability Using an Index Based on Residual Expansion", Thesis, Clemson University (2002).

Table 40: Physical Properties and Freezing and Thawing Performance

Mix	28 Day Compressive Strength	28 DayTensile Strength 228	Survival in C666 Number of Cycles
C	768	116	≈50
1	197	51	≤6
2	563	43	≤6
3	472	68	≤6
4	516	52	≤6
5	381	59	≤6
6	678	44	≤24
7	481	65	≤24 (Slightly better than Mix 6)

Since the highest strength mortar mix was the mix with the highest cement content, it appears that high cement content is an essential consideration for restoration and repair. Further, since lime additions diminish the strengths of the mortars, restoration and repair mortars with natural cement where freezing and thawing performance is important and should contain the minimum lime content as may be required to achieve workable mortar. Interestingly, the water content of pointing mortars, i.e. manual pointing versus grout bag consistency, did not affect freezing and thawing performance.

Researchers working with porous materials and observing their freezing and thawing performance when the materials are saturated with water always observe that the performance is variable or "statistical" in nature. Observations in this research were made on three specimens in a specific testing environment (the C666 test). Paragraph 3.4 in C666 states, "No relationship has been established between the resistance to cycles of freezing and thawing of specimens cut from hardened concrete and specimens prepared in the laboratory." Therefore, these results should be viewed as relative for one mix compared to another.

Mechanical Properties of Masonry Assemblies

The purpose of testing masonry assemblies used in this research was to provide engineering data useful in structural design and modeling for the restoration mortars of this research. To that end, the flexural bond strengths and pier compressive strengths of the mortars were evaluated using a contemporary molded brick product (qualified under ASTM C216) in the test prisms. The properties of the molded brick are given in Table 41. Only mixes C and 2 were tested for flexural bond strength while Mix 2 was tested for pier compressive strength.

Table 41: Average Properties of the Molded Brick Used in Masonry Prism Tests (ASTM C67)

Property	Result
Cold water absorption, %	11.96
Boiling water absorption, %	16.59
Saturation coefficient	0.72
Compressive strength, lb./in^2	5412
Efflorescence (rating)	Not effloresced
Initial rate of absorption (IRA), g/30 in^2*min	73.8

Flexural Bond Strength

Flexural bond strength for restoration can be specified for restoration purposed according to ASTM C1713, *Standard Specification for Repairs for Mortars for Historic Masonry*. If specified, the masonry assembly must exhibit flexural bond strength of at least 29 lb./in^2 when tested according to the method in ASTM C1357, *Standard Test Methods for Evaluation of Masonry Bond Strength*. The test method for laboratory produced specimens in C1357 is given in ASTM C1072, *Measurement of Masonry Flexural Bond Strength*. The method in C1072 is usually called the "bond wrench".

One bond wrench test is shown in Figure 60 after one mortar joint has been tested to failure. After the test, the mortar is examined for mode of failure. The typical failure in this study was delamination of the mortar from the brick at the joint (Figure 61). Fragments of brick are shown in the separated mortar beds that were pulled away from the brick surface in the test. Flexural bond strength results are provided in Table 42. Both Mixes C and 2 exceed the minimum criterion in C1713.

Figure 60: Bond Wrench Test of Masonry Prism With Restoration Mortar (File 2166)

Figure 61: Mortar Joint after Failure in the Bond Wrench Test (File 2167)

Table 42: Flexural Bond Strength Results for Mixes C and 2

Mix C	Mix C	Mix C	Mix 2	Mix 2	Mix 2
Flexural Tensile Strength (psi)	**Failure Top of Joint**	**Failure Bottom of Joint**	**Flexural Tensile Strength** lb./in^2	**Failure Top of Joint**	**Failure Bottom of Joint**
13		x	111		x
36		x	92	x	
6		x	81	x	
17	x		73	x	
56		x	59		x
64		x	62		x
75		x	77		x
8	x		93		x
39		x	75		x
68	x		124		x
39		x	131	x	
51		x	119		x
24		x	83		x
xx		x	102		x
59		x	102	x	
14		x	113		x
36		x	84		x
6		x	113		x
13		x	67		x
25		x	122		x
Average 34			Average 94		

Pier Compressive Strength

The compressive strength of masonry prisms was determined according to ASTM C1314, *Standard Test Method for Compressive Strength of Masonry Prisms*. Note that this property is not a requirement of ASTM C1713, *Standard Specification for Repairs for Mortars for Historic Masonry*. Nevertheless, it is of vital interest in masonry design. Typical values are in the range of 1000-3000 lb./in^2 when the brick units exhibit a compressive strength greater than 3000 lb./in^2. A typical test using the restoration mortar Mix 2 is shown in Figure 62 with a prism at failure in Figure 63.

Figure 62: Test for Pier Compressive Strength (File 2168)

Figure 63: Failure in the Pier Compressive Test (File 2173)

The pier compression results are provided in Table 43 where the average is in the expected range of 1000-3000 lb./in^2. The failure modes are primarily face shell separation. Failure modes are provided in Figure 64.

Table 43: Pier Compressive Strength Results for Mix 2

Mortar	Failure Mode	Peak Load	Net Compressive Strength lb/in^2
2	7 or 4	83046	2649
2	7	76243	2433
2	7	80890	2554
2	4	71998	2243
2	7	67029	2106
2	7	72859	2362
2	7	78198	2531
2	7	74890	2415
		Average	2412

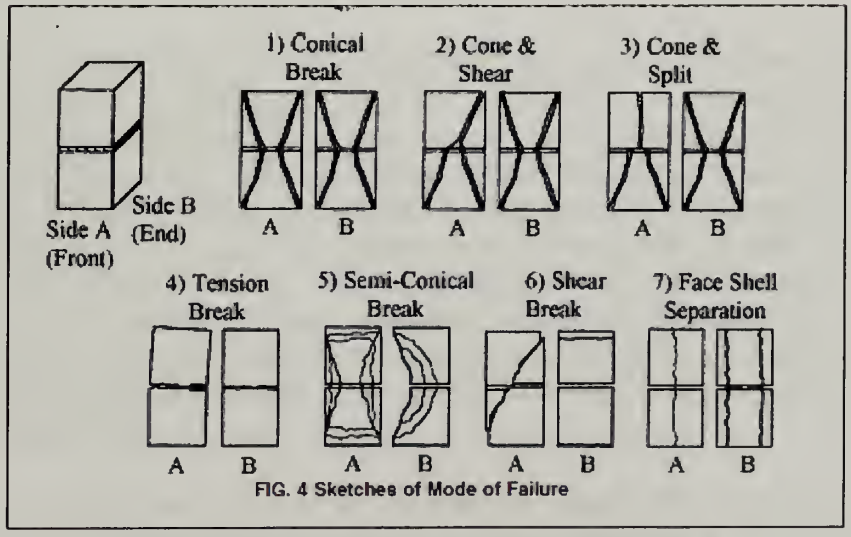

Figure 64: Failure Modes in ASTM C1314

Conclusions

The major focus of this research was determining the chemical solution or leaching by sea water from restoration mortars for use at Fort Sumter National Monument (FSNM) and for other masonry structures such as Third System fortifications and lighthouses built during the era of natural cement construction in the United States (roughly 1840-1900). The results are also germane to salt interaction in mortars resulting from masonry saturation by rising damp.

Initial activities included characterization of materials and formulation of restoration mortars. Following historic practices, all restoration mortars were produced at a ratio of one part fine material (cement or cement and lime) and sand. Early experiments found practical limitations within the fine materials of a maximum ratio of one part of lime to one part of cement to achieve practically useable setting rates of five days or less. Therefore, mixes tested in this research either contained no lime or one half part of lime per part of cement or one part of lime per part of cement by volume.

It is well known in masonry art that lime adds workability to mortars providing properties for spreading materials in construction of masonry wall elements or in repair of walls by pointing. It was particularly evident in this study that even a small amount of lime adds to workability and mortar board life – essential attributes for any restoration mason. Nevertheless, lime has been shown to deleteriously affect other masonry properties, as discussed below. Therefore, there are compromises between composition and performance that are especially important when salts can intrude into masonry during its life.

Rosendale cement was the only natural cement included in experiments because of its use at FSNM. This cement is calcined (heated) and produced from dolomitic limestone but with incomplete carbonate decomposition, i.e. it is not a completely "reacted" or fused cement such as contemporary portland cement. The Rosendale cement was found to contain major phases of calcite ($CaCO_3$), quartz (SiO_2), periclase (MgO), and glass. A minor phase of Portlandite or $Ca(OH)_2$ was found to vary between separate lots of Rosendale cement possibly explaining differences in setting rates between lots. The Rosendale cement was also found to contain carbonated phases of calcium silicate suggesting carbonation in situ after manufacture. For restoration purposes, Rosendale cement that might have been held in local inventory for a long time may require testing of the setting rate to insure it meets the criteria in ASTM C10, the standard for natural cement.

There was significant effort in this research to chemically and physically characterize mortars produced for sea water corrosion testing, and the techniques used should serve as a guide for restoration professionals. For example, thermal analysis techniques were used to facilitate specimen compositional calculations to verify that the specimens as-produced in the laboratory actually met the goals in the experimental plan. The mortars were characterized as to their compressive strength and tensile strength to compliment contemporary restoration research in other projects. It was found that the mortars for restoration at FSNM made with ASTM "graded sand" (to mimic the original mortars used) had slightly lower strength than mortars made according to ASTM Standard mixes that contain coarser "20-30" sand. The mortars of this study had greater water vapor transmissions than recently reported for Type N and O masonry mortars

containing portland cement, mortars frequently used in restoration work. This is a desired result, as all restoration mortars should not contribute to water accumulation in masonry.

It was found that the mortars of this study selectively absorb or "take up" ions of magnesium, chloride, and sulfate when immersed in sea water, but they also dissolve or leach species of calcium, potassium, and sodium on sea water immersion. All of the mortars of this study exhibited weight loss indicative of corrosion loss in sea water, with mixes containing no lime exhibiting the highest corrosion loss. By contract, the mixes only containing Rosendale cement and sand exhibited the lowest calcium solution on sea water immersion.

A central issue for restoration mortars used where salt intrusion is likely is calcium solution, as calcium solution has been shown to cause "brick scaling" or cryptoflorescence damage to bricks in the masonry walls. This was particularly noted at FSNM on faces of the structure pointed with Type O masonry mortar in the past that are now exhibiting significant scaling damage. Since most strategies include a mandate to "do no harm" in restoration, the lowest calcium leaching or loss in the presence of sea water intrusion is a very significant criterion. Therefore, Rosendale-sand mortars might exhibit somewhat shorter life than Rosendale-lime-sand mortars, but the lime free mortars are preferred for restoration since they have the lowest potential to cause brick wear by scaling.

Restoration specialists have long recognized that it is a mistake to use "hard" portland cement containing mortars in pointing repair of "soft" historic bricks, as this practice results in facial disintegration of the old bricks. Technically, this is due to a mismatch in the elasticity of the repair and original mortars as judged by the property of Modulus of Elasticity. This concern is valid regardless of the presence of intruding salts. Now, this research has shown a chemical leaching criterion of importance for restoration to use in concert with consideration of Modulus of Elasticity of repair mortars.

The leaching criterion is of particular importance in restoration using modern masonry cement mortars and mortar cements. Care is advised when considering use of masonry cements and/or mortar cements in restoration due to the fact that these materials may exhibit excessive calcium solution over that normally observed in the setting of portland cement.

Tests of masonry assemblies were performed to make this research useful to structural engineers for design and modeling purposed. These values for mortared assemblies were comparable to those in ASTM Specifications and/or those reported in the engineering literature.

The research strongly suggests that mortars with high contents of Rosendale cement and with minimal lime in their composition exhibit superior resistance to freezing and thawing as compared to mortars with lower cement content or those gauged with more than a *de minimis* content of lime (as considerably less than one quarter part of lime to one part of cement). Therefore, optimal mortar compositions with natural cement for sea or ground water contact are the same as those for frost prone geographic zones.

The results of this research are in agreement with knowledge gained through the ages in those rare situations where masonry is usually immersed in sea water. For example, in Venice (Italy) pozzolanic or natural cement have been used in restoration in areas of sea water impingement and in areas of rising damp with lime mortars used in higher building elevations for restoration. For Third System fortifications, lighthouses, and other structures where salt intrusion is likely and where Rosendale cement is preferred for restoration, the mortars should contain little or no lime to ensure no harm to the bricks in the masonry structure.